

# **SALT EFFECT ON LIQUID LIQUID EQUILIBRIUM OF THE SYSTEM WATER + 1-BUTANOL + ACETONE AT 298K: EXPERIMENTAL DETERMINATION**

A Thesis Submitted

*By*

**SITANSU PALEI**

(Roll No. 10600015)

In partial fulfillment for the award of the Degree of

**BACHELOR OF TECHNOLOGY**

**IN**

**CHEMICAL ENGINEERING**

*Under the esteemed guidance of*

**Dr. P RATH**



**Department of Chemical Engineering**

**National Institute of Technology Rourkela**

**2010**



National Institute of Technology Rourkela

## CERTIFICATE

This is to certify that the thesis entitled, “**Salt effect on LLE of the system water + 1-butanol + acetone at 298k: experimental determination**” submitted by **Sitansu Palei** for the requirements for the award of Bachelor of Technology in Chemical Engineering at National Institute of Technology Rourkela, is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the seminar report has not been submitted to any other University / Institute for the award of any Degree or Diploma.

**Dr. P RATH**

Professor

**Date:**

Department of Chemical Engineering

National Institute of Technology Rourkela

# ACKNOWLEDGEMENT

I would like to make my deepest appreciation and gratitude to Dr. P Rath for his valuable guidance, constructive criticism and encouragement during every stage of this project. I am totally indebted to him for providing me the right guidance to work on an emerging area of chemical engineering. He was very supportive throughout the project and was always ready to help.

Thanks to Dr. R K Singh and Dr. H M Jena for being uniformly excellent advisors. They were always very helpful and provided broad ideas.

I owe a depth of gratitude to Prof. S. K. Agarwal, H.O.D, Department of Chemical Engineering, for all the facilities provided during the course of my tenure.

Lastly I would like to thank my family members for their constant support, encouragement and good wishes, without which this thesis wouldn't have been possible.

**Sitansu Palei**

**Date:**

## **ABSTRACT**

The influence of a solid salt on VLE and LLE cannot be ignored because it significantly changes the equilibrium composition. Liquid-Liquid Equilibrium is the result of intermolecular forces which can significantly change due to salt addition which introduces ionic forces, affecting the thermodynamic equilibrium. Aqueous electrolyte liquid-liquid equilibrium is often related to extraction processes. In the present work the salt effect on the system namely '1-Butanol+Water+Acetone' has been studied with various salts under varied concentration at 298K. The salt used in the above system are NaCl, KCl with 5%, 10% and 15% concentration. The solubility data and tie-line data are taken experimentally at different salt concentration. The experimentally determined tie-line data of this work have been correlated by Hand's correlation.

**KEYWORDS:** Liquid-liquid equilibrium; Data; Salt effect; Experimental; Correlation

# CONTENTS

| TITLE  | PAGE NO. |
|--|----------|
| Abstract   | iv       |
| List of Symbols  | vii      |
| List of figures  | viii     |
| List of Tables   | xi       |
| Chapter 1:   |          |
| 1.1 Introduction                                       | 1        |
| 1.2 Importance & Application                           | 1        |
| 1.3 Objective of the present work                      | 2        |
| 1.4 Liquid Liquid Equilibrium                          | 2        |
| 1.5 Salt effect on LLE                                 | 3        |
| 1.6 Salting-in & Salting-out                           | 4        |
| Chapter 2:   |          |
| 2 Effect of salt on LLE                                | 5        |
| 2.1 Salt effect on LLE (Table 1)                       | 5        |
| 2.2 Systems studied under present work                 | 11       |
| Chapter 3:   |          |
| 3 Introduction for Experiment                          | 12       |
| 3.1 Material used                                      | 12       |
| 3.2 Physical Properties of solvent used                | 12       |
| 3.3 Experimental set up                                | 13       |
| 3.4 Procedure for solubility data for ternary liquid   | 14       |
| System   |          |
| 3.5 Solubility data for salt containing ternary liquid | 14       |

## System

|   |         |
|---|---------|
| 3.6 Measurement of equilibrium data for ternary | 14      |
| Liquid mixture with and without a salt          |         |
| 3.7 Method of analysis                          | 15      |
| Chapter 4:                                      |         |
| 4. Presentation of result                       | 16      |
| 4.1 Empirical Correlation of salt effect on LLE | 16      |
| 4.2 (a) All the figures                         | 18 – 34 |
| (b) All the plots                               | 35 – 43 |
| (c) All the Tables                              | 44 – 54 |
| 4.3 Results and Discussion                      | 55      |
| Chapter 5:                                      |         |
| Conclusion                                      | 56      |
| References                                      | 57      |

## LIST OF SYMBOLS

|          |   |
|----------|---|
| A        | Water   |
| B        | 1 – Butanol   |
| C        | Acetone   |
| $X_A$    | Mass fraction of Water                                    |
| $X_B$    | Mass fraction of 1-Butanol                                |
| $X_C$    | Mass fraction of Acetone                                  |
| $X_{AA}$ | Mass fraction of Water in Water layer                     |
| $X_{AB}$ | Mass fraction of Water in Butanol layer                   |
| $X_{BA}$ | Mass fraction of 1-Butanol in Water                       |
| $X_{BB}$ | Mass fraction of 1-Butanol in 1-Butanol layer             |
| $X_{CA}$ | Mass fraction of Acetone in Water                         |
| $X_{CB}$ | Mass fraction of Acetone in Butanol layer                 |
| $X_S$    | Salt Percentage   |
| a,b,c,d  | Constants for Eisen-Joffe and Modified Campbell Equation. |
| Ln A, B  | Constants for Hand's Plot                                 |

## LIST OF FIGURES

| Fig No. | Contents   | Page No. |
|---------|--|----------|
| 1       | Schematic diagram of LLE apparatus   | 18       |
| 2       | Schematic diagram for evaporation of liquid mixture  | 19       |
| 3       | Triangular Diagram   | 20       |
| 4       | Plot of refractive index vs. Mass fraction of acetone<br>For no salt condition (Aqueous Phase) | 21       |
| 5       | Plot of refractive index vs. Mass fraction of acetone<br>For no salt condition (Organic Phase) | 21       |
| 6       | Plot of refractive index vs. Mass fraction of acetone<br>For 5% NaCl. (Aqueous Phase)          | 22       |
| 7       | Plot of refractive index vs. Mass fraction of acetone<br>For 5% NaCl. (Organic Phase)          | 22       |
| 8       | Plot of refractive index vs. Mass fraction of acetone<br>For 10% NaCl. (Aqueous Phase)         | 23       |
| 9       | Plot of refractive index vs. Mass fraction of acetone<br>For 10% NaCl. (Organic Phase)         | 23       |
| 10      | Plot of refractive index vs. Mass fraction of acetone<br>For 15% NaCl. (Aqueous Phase)         | 24       |
| 11      | Plot of refractive index vs. Mass fraction of acetone  | 24       |



|    |   |    |
|----|---|----|
|    | For 15% NaCl. (Organic Phase)                         |    |
| 12 | Plot of refractive index vs. Mass fraction of acetone | 25 |
|    | For 5% KCl. (Aqueous Phase)                           |    |
| 13 | Plot of refractive index vs. Mass fraction of acetone | 25 |
|    | For 5% KCl. (Organic Phase)                           |    |
| 14 | Plot of refractive index vs. Mass fraction of acetone | 26 |
|    | For 10% KCl. (Aqueous Phase)                          |    |
| 15 | Plot of refractive index vs. Mass fraction of acetone | 26 |
|    | For 10% KCl. (Organic Phase)                          |    |
| 16 | Plot of refractive index vs. Mass fraction of acetone | 27 |
|    | For 15% KCl. (Aqueous Phase)                          |    |
| 17 | Plot of refractive index vs. Mass fraction of acetone | 27 |
|    | For 15% KCl. (Organic Phase)                          |    |
| 18 | Solubility curve for no salt condition                | 28 |
| 19 | Solubility curve for 5% NaCl                          | 29 |
| 20 | Solubility curve for 10% NaCl                         | 30 |
| 21 | Solubility curve for 15% NaCl                         | 31 |
| 22 | Solubility curve for 5% KCl                           | 32 |
| 23 | Solubility curve for 10% KCl                          | 33 |
| 24 | Solubility curve for 15% KCl                          | 34 |
| 25 | Distribution curve for NaCl                           | 35 |
| 26 | Distribution curve for KCl                            | 35 |
| 27 | Campbell's plot for NaCl                              | 36 |
| 28 | Campbell's plot for KCl                               | 36 |
| 29 | Hand's Plot for NaCl                                  | 37 |

|    |   |    |
|----|---|----|
| 30 | Hand's Plot for KCl   | 37 |
| 31 | Experimental vs. Calculated values of mass fraction of<br>Acetone (for NaCl) (Campbell Equation)      | 38 |
| 32 | Experimental vs. Calculated values of mass fraction of<br>Acetone (for KCl) (Campbell Equation)       | 38 |
| 33 | Experimental vs. Calculated values of mass fraction of<br>Acetone (for NaCl) (Eisen – Jeffe Equation) | 39 |
| 34 | Experimental vs. Calculated values of mass fraction of<br>Acetone (for KCl) (Eisen – Jeffe Equation)  | 39 |
| 35 | Determination of Log A & B for NaCl (Campbell Equation)   | 40 |
| 36 | Determination of Log A & B for KCl (Campbell Equation)  | 41 |
| 37 | Determination of Log A & B for NaCl(Hand's Equation)  | 42 |
| 38 | Determination of Log A & B for KCl(Hand's Equation)   | 43 |

## LIST OF TABLES

| Table No.  | Contents  | Page No. |
|------------|---|----------|
| 1          | List of Some Previous Investigation on Salt effect on LLE | 5        |
| 2          | List of system studied related present work               | 11       |
| 4.1.1      | Solubility Data for no salt condition                     | 44       |
| 4.1.2(i)   | Solubility Data for 5% NaCl                               | 44       |
| 4.1.2(ii)  | Solubility Data for 10% NaCl                              | 45       |
| 4.1.2(iii) | Solubility Data for 15% NaCl                              | 45       |
| 4.1.3(i)   | Solubility Data for 5% KCl                                | 45       |
| 4.1.3(ii)  | Solubility Data for 10% KCl                               | 46       |
| 4.1.3(iii) | Solubility Data for 15% KCl                               | 46       |
| 4.2.1      | Equilibrium Data for No salt condition                    | 47       |
| 4.2.2(i)   | Equilibrium Data for 5% NaCl                              | 47       |
| 4.2.2(ii)  | Equilibrium Data for 10% NaCl                             | 48       |
| 4.2.2(iii) | Equilibrium Data for 15% NaCl                             | 48       |
| 4.2.3(i)   | Equilibrium Data for 5% KCl                               | 49       |
| 4.2.3(ii)  | Equilibrium Data for 10% KCl                              | 49       |
| 4.2.3(iii) | Equilibrium Data for 15% KCl                              | 50       |
| 4.3.1      | Constants Ln A & B in modified Campbell Equation          | 51       |
| 4.3.2      | Constants Ln A & B in Hand's Plot                         | 51       |
| 4.4.1      | Constants a, b, c and d in modified Campbell Equation     | 52       |
| 4.4.2      | Constants a, b, c and d in Eisen – Joffe Equation         | 52       |

|       |   |    |
|-------|---|----|
| 4.5.1 | Comparison between $X_{CB}$ – Experimental vs. $X_{CB}$ – Calculated<br>For NaCl. | 53 |
| 4.5.2 | Comparison between $X_{CB}$ – Experimental vs. $X_{CB}$ – Calculated<br>For KCl   | 54 |

## CHAPTER-1

### 1.1 INTRODUCTION

Aqueous solutions containing salts are of increasing importance and influence on separation processes in chemical engineering. The electrolyte influence must be considered both in process design and operation, because it can significantly change the equilibrium composition. Aqueous liquid–liquid equilibrium is the results of intermolecular forces, mainly of the hydrogen–bonding type; addition of a salt to such systems introduces ionic forces that affect the thermodynamic equilibrium. When the mutual solubility decreases due the salt addition, the size of the two–phase region increases, and this effect is called “salting-out”. In the opposite, when the solubility increases, the effect is called “salting-in”. The salting–in effect can be used to remove organic compounds from water. [6]

Aqueous electrolyte liquid–liquid equilibrium is often related to extraction processes. For instance, the ethyl acetate recovery from its mixture with ethanol involves an aqueous extraction step in order to remove the ethanol. In this case, it is important to decrease the mutual solubility’s of water and ester, improving the separation and yielding a dryer ester. [6]

The separation by solvent extraction becomes increasingly more difficult as the tie-line becomes parallel to the solvent axis, as shown in solutropic solutions. By adding an adequate salt, the mutual solubility of the mixture can be significantly changed, in order to modify the slope of the tie-lines, even to the extent of eliminating the solutrope. [6]

The presence of an electrolyte in a solvent mixture can significantly change its equilibrium composition. The concentration of a solvent component in a liquid phase of liquid-liquid system increases if component is salted in and decreases if it is salted out of the liquid phase. This salt effect has been advantageously used in solvent extraction. Separation by solvent extraction becomes increasingly more difficult as the tie-lines become parallel to the solvent axis as in the case of solutropic solution. By adding a suitable salt the tie-line of a LLE mixture can be significantly changed, even to extent of eliminating the solutrope.

### 1.2 IMPORTANCE AND APPLICATION

The addition of an electrolyte to solvent mixtures changes the interaction among the various solvent and solute molecules resulting in shifting their phase equilibrium even to the extent of eliminating solutrope in liquid equilibrium. In an aqueous-organic solvent mixture, addition

of an electrolyte generally salts out the organic solvent molecules thus enriching the organic phase with organic solvent component resulting in considerable reduction of the energy cost incurred in the recovery and purification of the organic solvent.

**Application of salting in effect:** Salting in occurs when, for instance, a polar solvent is added to an aqueous salt solution and is preferentially solvents the water and hence breaks the hydration cages previously formed around the salt ions. The may be used to recover salts from concentrated aqueous solution, and it is also important in biological separation process such as purification of proteins, enzymes, nucleic acids and others.[2]

**Application of Salting out effect:**

1. Recovery of tightly hydrogen bonded organics from water such as formaldehyde, formic acid and acetic acid by using ionic salt.
2. Biphasic mixtures containing of two immiscible phases are separated by use of salt like ionic salt.
3. Mixture having non polar solvent +polar solvent + water, then salt is used to separate the solution.

### 1.3 OBJECTIVE OF THE PRESENT WORK

In this project, a suitable correlation was suggested for application in industrial extraction process involving water + solute + solvent + electrolyte systems. The correlation has to be able to give an accurate description of liquid-liquid equilibrium that is important for solvent extraction process. The present system comprises the following components.

**Water+1-Butanol+Acetone**

The main objective of the present work is to suggest a suitable correlation for the salt effect.

### 1.4 LIQUID-LIQUID EQUILIBRIUM

**Triangular diagrams:**

Liquid-liquid extraction involves the use of systems composed of at least three substances, and in most cases all three components appear in both insoluble phases. Ternary systems are often represented on equilateral or right triangular coordinates.

Triangular diagrams (fig. 3) are used for representing three component systems. Every possible composition of the ternary mixture corresponds to a point in the diagram. Each

corner of the triangle represents a pure component and its designation is marked at this corner. On the side opposite to this corner the mass fraction of this component is zero. In this diagram the left vertex represent as diluents, right vertex as solvent and the top as solute. The sides of the triangle represent the corresponding two-component system.

The sum of the vertical distances to the three sides from any point within the triangle is also equal to 100 percent, from geometrical considerations.

If the quantities of diluents, solvent and solute present in a ternary mixture are such that two phases exist, each phase is said to be mutually saturated. A plot of the compositions of the two individual phases when in equilibrium with each other gives a mutual solubility curve. Only ternary systems with miscibility gaps are suitable for extraction, and the boundary line between the liquid single-phase region and two-phase region is particularly important. This boundary line is called the binodial curve. Every point in the binodial curve is in equilibrium with another binodial point. The lines, which connect points in equilibrium with one another, are called tie-lines. All mixture, which correspond to a point on the tie line separate into two phases.

### 1.5 SALT EFFECT ON LLE

Salt has a great effect on LLE. The addition of non-volatile solute to a solvent mixture changes the interaction among the various solvent solutes molecules resulting in shifting their phase equilibrium even to the extent of eliminating the solutrope in LLE. The salt mainly affects the solubility of organic component in an aqueous-organic solvent mixture. Addition of an electrolyte generally salts out the organic solvent molecules thus enriching the organic in organic phase with organic solvent component resulting in considerable reduction of the energy cost incurred in the recovery and purification of organic solvent. The distribution of solute between two liquid phases mainly depends upon the concentration of electrolyte. The electrolyte will remain in the phase in which it is most soluble and the other solute will be transferred to the phase that it is poor in electrolyte. In other cases the addition of salt to a solvent mixture can cause a phase split in a system that did not show demixing, this treatment is sometimes used to enable separation by liquid extraction. Many liquid-liquid system exhibits the solutropy and the phenomena in which the solute favours one phase at low solute concentration other at higher solute concentration. A change in the behaviour of the solutropy system is expected when salt is added in the system.

Selectivity, it is the process of removal of solute preferentially over water, which is significantly affected by the salt present in the system. The selectivity, which is a ratio of

distribution coefficient of solute to that of water, is changed much more by salt addition than is the distribution coefficient of the solute alone. The lower distribution coefficient of water can be attributed to the association of water molecule in unextracted slating the aqueous phase, which impedes a transfer of water to the organic phase. From practical point of view resulting higher selectivity means a good separation.

## 1.6 SALTING OUT & SALTING IN

### SALTING OUT:

Salting out can also be explained by the fact that when the ions are solvated, some of the water becomes unavailable for solute which is then salted out from the aqueous phase. This can be exploited to remove organic compounds from water. The term salting out is used since if salt is added to a saturated solution of a non-electrolyte in water, the result is to bring the non-electrolyte out of solution. [2]

### SALTING IN:

Salting in occurs when, for instance, a polar solvent is added to an aqueous salt solution and is preferentially solvents the water and hence breaks the hydration cages previously formed around the salt ions. This may be used to recover salts from concentrated aqueous solution, and it is also important in biological separation process such as purification of proteins, enzymes, nucleic acids and others. [2]



## CHAPTER - 2

### LITERATURE REVIEW

#### 2. EFFECT OF SALT ON LLE

A lot of authors have worked on liquid-liquid equilibrium system. But few of them worked on the salt effect on LLE. It is observed that the use of salt has been proven advantageous. In this review developments and trends are outlined with emphasis on existing correlation. The literature relating to the industrial application with such a salt effect is described.

##### 2.1 Salt effect on LLE

Table-1

| Serial number | Literature   | System studied  | Salt used                  | Results   |
|---------------|--|---|----------------------------|---|
| 1             | Hasseine A.,<br>Meniai A H,<br>Korichi M,<br>salting out<br>effect of single<br>salt on LLE,<br>science direct,<br>Desalination<br>242 (2009) pp-<br>264-276 [2] | Water+acetone+tolune<br>Water+cyclohexane+2-<br>propanol<br>Water+xylene+methanol | NaCl, KCl                  | Salting out effect<br>is more prounced<br>with NaCl<br>compared to<br>KCl, due to<br>difference in<br>hydration<br>energies.  |
| 2             | Bourayou N.,<br>Meniai A H,<br>Influence of<br>salt on liquid<br>phase equilibria<br>for totale<br>miscible<br>organic<br>compound with<br>water, science        | Water+acetone<br>Water+propanol   | NaCl,<br>CaCl <sub>2</sub> | The addition of<br>two salts has<br>shifted the<br>systems from<br>being totally<br>homogeneous to<br>heterogeneous<br>one. This has<br>great application<br>in phase |

|   |  |   |                                     |   |
|---|--|---|-------------------------------------|---|
|   | direct,<br>Desalination<br>185 (2005) pp-<br>473-481 [4]   |   |                                     | separation<br>process.  |
| 3 | Hu Mancheng,<br>Wang Meixia,<br>Li Shu ni,<br>Jiang Yucheng,<br>Guo Haiyan,<br>LLE for<br>Quaternary<br>systems at<br>298.1K,<br>science<br>direct,fluid<br>phase<br>Equilibria 263<br>(2008) pp-109-<br>114. [10] | Water+1-propanol<br>Water+2-propanol        | KCl, CsCl                           | Influences of the<br>inorganic salts<br>and aliphatic<br>alcohols on the<br>LL region, in<br>short, the<br>different<br>salvation abilities<br>and solubilities<br>of KCl, CsCl and<br>the different<br>polarities of the<br>two alcohols<br>affected the<br>results. |
| 4 | Chen Jui Tang,<br>Chen Ming-<br>Chung, salting<br>effect on LLE<br>for the ternary<br>system, science<br>direct, Fluid<br>Phase<br>Equilibria<br>266(2008), pp-<br>1-7. [3]  | Water+N-methyl-2-<br>pyrrolidone+1-pentanol | NaCl, KCl,<br>CH <sub>3</sub> -COOK | The liquid phase<br>splitting for<br>ternary system of<br>water+N-methyl-<br>2-pyrrolidone+1-<br>pentanol can be<br>enhanced by<br>adding the same<br>percentage of<br>salts and the<br>influence follows<br>the order of<br>NaCl>KCl>KAc.                            |
| 5 | Santos G. R,   | Water+Ethanol+1-                            | KBr                                 | The addition of   |

|   |  |  |     |  |
|---|--|--|-----|--|
|   | d'Avila S.G,<br>Aznar M., salt<br>effect on LLE,<br>Brazilian<br>journal of<br>chemical<br>engineering,<br>Vol. 17,<br>(2000),pp-721-<br>734. [11]   | Pentanol   |     | bromide<br>potassium<br>improves ethanol<br>extraction by<br>means of 1-<br>pentanol. The<br>improvement<br>result from salt<br>effect, which<br>modifies the<br>phase<br>equilibrium of<br>the mentioned<br>system,<br>increasing the<br>distribution<br>coefficient for<br>ethanol and<br>selectivity of the<br>solvent. |
| 6 | Tan T.C.,<br>Kannangare<br>k.K.D.D.S.,<br>Liquid-liquid<br>equilibrium of<br>a system in<br>preence of salt,<br>science direct,<br>fluid phase<br>Equilibrium<br>190 (2001) pp-<br>179-189. [12] | Water+1-propanol<br>Water+1-<br>propanol+methyl-ethyl-<br>ketone | KCl | Although methyl<br>ethyl ketone is a<br>reasonably good<br>solvent for<br>solvent<br>extraction of 1-<br>propanol from its<br>aqueous mixture,<br>its extractive<br>efficiency can be<br>further and<br>considerably<br>enhanced with  |

|  |  |  |  |   |
|--|--|--|--|---|
|  |  |  |  | the addition of KCl into the solvent mixture. |
|--|--|--|--|---|

| Serial number | Literature  | System studied                     | Salt used | Results   |
|---------------|---|------------------------------------|-----------|---|
| 7             | Solimo Horacio N.,<br>Bonatti Carlos M.,<br>Zurita Jose L., de Doz<br>Monica B. Gramajo,<br>salt effect on<br>LLE,Elsevier, Fluid-<br>Phase Equilibria137<br>(1997) pp-163-172.<br>[13] | Water+propanoic<br>acid+1-butanol. | NaCl      | The presence of the salt decreases the solubility of the system, increasing the heterogeneous zone. The experimental results lead to the conclusion that a salting-out effect is present at all studied NaCl concentrations, increasing for |

|   |   |                             |           |   |
|---|---|-----------------------------|-----------|---|
|   |   |                             |           | higher salt concentrations.   |
| 8 | R. Pedraza, F. Ruiz, M.D. Saquete, V. Gomis, Liquid-liquid-solid equilibrium for quaternary system, Science direct, Fluid Phase Equilibria 216 (2004) 27–31. [14] | Water+1-butanol+2 salts     | NaCl, KCl | The liquid–liquid tie lines obtained have been used to check the accuracy of the predictions using the electrolyte NRTL model (MNRTL). The model is useful for the calculation of the liquid–liquid equilibrium data of quaternary systems using parameters obtained by correlation of some Of the ternary systems that constitutes it. |
| 9 | Tan T.C., Aravindh S., Salt effect on LLE, Elsevier, Fluid Phase Equilibria   | Water+acetic acid+1-butanol | NaCl, KCl | Both sodium and potassium chloride increased the  |

|    |  |   |           |   |
|----|--|---|-----------|---|
|    | 163(1999).243–257.<br>[15]   |   |           | area of the two-phase region and decreased the Mutual solubilities of 1-butanol and water. Both marginally decreased the concentration of 1-butanol and acetic acid in the aqueous phase while significantly increased their concentrations in the organic Phase. |
| 10 | Vakili-Nezhaad G.R.,<br>Mohsen-Nia M.,<br>Taghikhani V.,<br>Behpoor M.,<br>Aghahosseini M.,<br>Salting out effect of salts on ternary LLE data, Science direct, J. Chem. Thermodynamics 36 (2004) 341–348. [7] | (water+propionic acid+isopropyl methyl ketone)<br>(water+propionic acid+isobutyl methyl ketone) | NaCl, KCl | The results showed that the electrolytes significantly affect the solubility of Propionic acid In the organic solvents used. The results also showed that the distribution  |

|  |  |  |  |   |
|--|--|--|--|---|
|  |  |  |  | coefficients for Propionoic acid and the selectivity of the organic solvents in extracting Propionoic acid increase in the presence of electrolytes in the ternary systems. |
|--|--|--|--|---|

## 2.2 SYSTEM STUDIED UNDER PRESENT WORK

| Literature   | System Studied          | Salt Used                    | Remarks  |
|--|-------------------------|------------------------------|--|
| Santos Fania S.,<br>d'Avila Saul G.,<br>Aznar Martin, salt effect on liquid-liquid equilibrium of water + 1-butanol + acetone:<br>experimental determination and thermodynamic modeling, science direct, fluid phase equilibria 187-188 (2001) 265-274.[6] | Water+1-Butanol+Acetone | NaCl, CH <sub>3</sub> -COONa | Electrolyte LLE data of quaternary systems at 20 and 40 <sup>0</sup> c or experimentally determined by chromatographic and gravimetric analysis .the effect of the salt addition on the original ternary system was observed by the increase of two phase region and the changes in the slope of the experimental tie lines. |

## CHAPTER - 3

### EXPERIMENTAL PROCEDURE AND SET UP

#### 3. INTRODUCTION

The experimental measurement of liquid-liquid equilibrium must achieve two things.

- It must locate the position of the solubility curve and
- It must determine the composition of the coexisting phases, which locate the ends of the tie lines.

In some cases these two objectives can be achieved in one measurement, and in other cases, two sets of measurement are necessary. In the first case, for a ternary system mixtures of three component are allowed to separate into its conjugate phases at equilibrium and the equilibrate layers are analysed for their composition which will give the end points of the tie lines. These end points when connected will give the binodial curve. This method is called the method of analysis. The second method involves the estimation of binodial curve and the tie lines in two stages, which is measured separately. [18, 21]

#### 3.1 Materials Used:

##### Chemicals and salts used:

- 1-Butanol
- Acetone
- Water
- Anhydrous NaCl (dried)
- Anhydrous KCl (dried)

#### 3.2 PHYSICAL PROPERTIES OF SOLVENT USED

| Components | Boling point ( $^{\circ}\text{C}$ ) | Melting point(K) | Molecular Wt.(gm) | Density(Gm/ml) |
|------------|-------------------------------------|------------------|-------------------|----------------|
| Acetone    | 56.53                               | 178              | 58.08             | 0.79           |
| 1-Butanol  | 117                                 | 183              | 74.12             | 0.81           |
| Water      | 100                                 | 273              | 18.015            | 1              |



### 3.3 EXPERIMENTAL SET UP

Experimental set up used for the determination of solubility data and tie line determination.

Apparatus required:

- Jacketed burette
- LLE apparatus
- Magnetic stir bar
- Thermometer
- Syringe
- Refractometer

**Jacketed Burette:**

A Pyrex 50ml burette, provided with a jacket for water circulation from the thermostat was used for titration in the determination of solubility data.

**LLE apparatus:**

It is jacketed cell water is flowing in the jacketed portion to maintain a constant temperature for proper working of reaction. A thermometer is inserted in the inner cell to measure the temperature. The prepared solution is fed into the inner cell, where it under goes proper mixing with salt in presence of a magnetic stir bar.

**Magnetic stir bar:**

It is used for proper mixing of salt and prepared solution in the presence of magnetic field in the inner cell. The stirring is continued for 2 to 3 hours.

**Thermometer:**

It is a mercury glass thermometer. It is used to measure the temperature of water in the inner cell.

**Syringe:**

It is used to draw liquid phase sample from the opening at the top sampling port to avoid cross contamination by other phase during the sampling process.

**Refractometer:**

It is used for the measurement of composition of phases at equilibrium.

### 3.4 PROCEDURE FOR SOLUBILITY DATA FOR TERNARY LIQUID SYSTEM:

A known quantity of a heterogeneous mixture (water varying from 1 to 20ml and the solvent varying from 20 to 1ml) was taken in a 100ml jacketed cell. Then the mixture was titrated with solute (acetone) taken in a jacketed burette. Water from the constant temperature bath was circulated through the jacket. The mixture was kept in constant stirring condition. The point of miscibility was noted. The end point, in this case, the disappearance of turbidity was noted. Then the refractive index of the mixture was measured by refractometer. The mass fraction of each component was calculated and tabulated. The above procedure was repeated for other specific mixture so as to cover entire range of composition. [18, 21]

### 3.5 SOLUBILITY DATA FOR SALT CONTAINING TERNARY LIQUID SYSTEMS:

The solubility data of a salt containing ternary system was determined by adopting the same experimental procedure used for salt free system, except that water was replaced by aqueous salt solution. The concentration of aqueous salt solution was varied from 5% to 15% of salt by mass; these concentrations were below saturation with respect to water. The solubility curve near the solvent rich region resulted in the precipitation of salt, which marked the disappearance of turbidity. Hence a complete solubility curve could not be obtained for the entire range of composition for the systems under this study. [18, 21]

### 3.6 MEASUREMENT OF EQUILIBRIUM DATA FOR LIQUID MIXTURE WITH AND WITHOUT A SALT:

A known heterogeneous ternary mixture was prepared by taking predetermined quantities of the three components (10ml solvent + 10ml diluents (water or salt solution of known concentration) + 1ml to 30ml of solute) in a 100ml jacketed cell. The mixture was thoroughly agitated for two hours by magnetic stirrer. After agitation, the mixture was allowed to stand for 2 hours to attain equilibrium. Two phases were found (i.e. raffinate & extract). The individual layer are separated by syringe and weighed. Then the refractive index of each layer was measured. In the case of dissolved salt each layer were boiled separately and condensed to make salt free and the refractive index of each layer were measured. The same technique was repeated for other known heterogeneous mixture. [18, 21]

### 3.7 METHOD OF ANALYSIS

There are many method used for analysis of equilibrium composition for ternary liquid liquid equilibrium system. These are as follows:

1. Titration method
2. Refractive index method
3. Gas chromatograph method
4. Specific gravity method

#### Refractive index method:

Equilibrium data of LLE for three components system is obtained by measuring refractive index of the solution using refractometer.

To find equilibrium data, known amount of three components corresponding to points within the binodial curve contained in stopper flasks, were agitated in the constant temperature bath over a period of 3 hours. At the end of this period the flasks were allowed to remain the bath until the phases had completely separated. The samples of the separated layers were withdrawn and their refractive indexes were measured. The composition of the equilibrium layers were found by references to a large scale plot of refractive index against solute concentration for saturated solution. In the case of dissolved salt each layer were boiled separately and condensed to make it salt free and then refractive index of each layer was measured.

## CHAPTER - 4

### 4. PRESENTATION OF RESULTS

This section represents the result of experimental work done. The solubility data with and without salt determined for above system are presented in table (4.1) as well as plotted in figure. The figures represent the smoothed values of solubility composition. The equilibrium tie line data are also presented in table (4.2). All salt containing data are reported on salt free basis. The experimental tie line data under no salt condition were determined and presented in their respective tables.

#### 4.1 EMPIRICAL CORRELATION OF SALT EFFECT ON LLE

The effects of salt on LLE of a ternary system have been widely studied. A lot of theories have advanced to explain the complex effect. However, the mathematical characterization of the salt effect has been semi quantitative at best, because of limitation of theories or inadequacy of assumptions made in the derivation of those equations. Hand and Othmer Tobias [16] have proposed equations to correlate tie line data of ternary liquid-liquid system under no salt condition. Setchenow, Eisen and Joffe [17] have proposed semi empirical models to correlate the tie line data of the ternary LLE under salt dissolved in the system. Setchenow [25] has proposed the following empirical equation for the salt effect on the distribution of solute between the relatively insatiable systems.

$$\ln(X_{CA}^0/X_{CA}) = K_S X_{SaA} \quad \text{----- (4.1)}$$

Where,  $K_S$  is a salt parameter.

According to Long and McDevit [21] have suggested the following equation which was derived on the basis of thermodynamic consideration

$$\ln(X_{CA}^0/X_{CA}) = K_S X_{SaA} + K_C(X_{CA} - X_{CA}^0) \quad \text{----- (4.2)}$$

Hand's equation [18, 20, and 24] for no salt condition is

$$\ln(X_{CB}/X_{BB}) = B \ln(X_{CA}/X_{AA}) + \ln A \text{ ----- (4.3)}$$

Eisen-Joffe [17, 20, and 24] equation is best on the adaptation of Hand's equation to system containing dissolved salts. In their model they have fitted Hand's constants  $\ln A$  and  $B$  in the following relations in the presence of salt, as a linear function of salt concentration.

$$\ln A = a + b X_S \text{ and } B = c + d X_S \text{ ----- (4.4)}$$

With the above relationships they have modified Hand's correlation into the following expression to suit the salt system. [20]

$$\ln(X_{CB}/X_{BB}) = (a + b X_S) + (c + d X_S) \ln(X_{CA}/X_{AA}) \text{ ----- (4.5)}$$

Where  $a$ ,  $b$ ,  $c$  and  $d$  are constants which depend on the nature of the system, nature of the salt and temperature, but are independent of salt concentration.

Recently Campbell [18, 23] proposed a correlation of ternary liquid system containing dissolved salts. The equation is as follows.

$$\ln(X_{CB}) = (a + b X_S) + (c + d X_S) \ln(X_{CA}) \text{ ----- (4.6)}$$

The present system is correlated by using Eisen - Joffe equation and Campbell equation for different salt concentration.

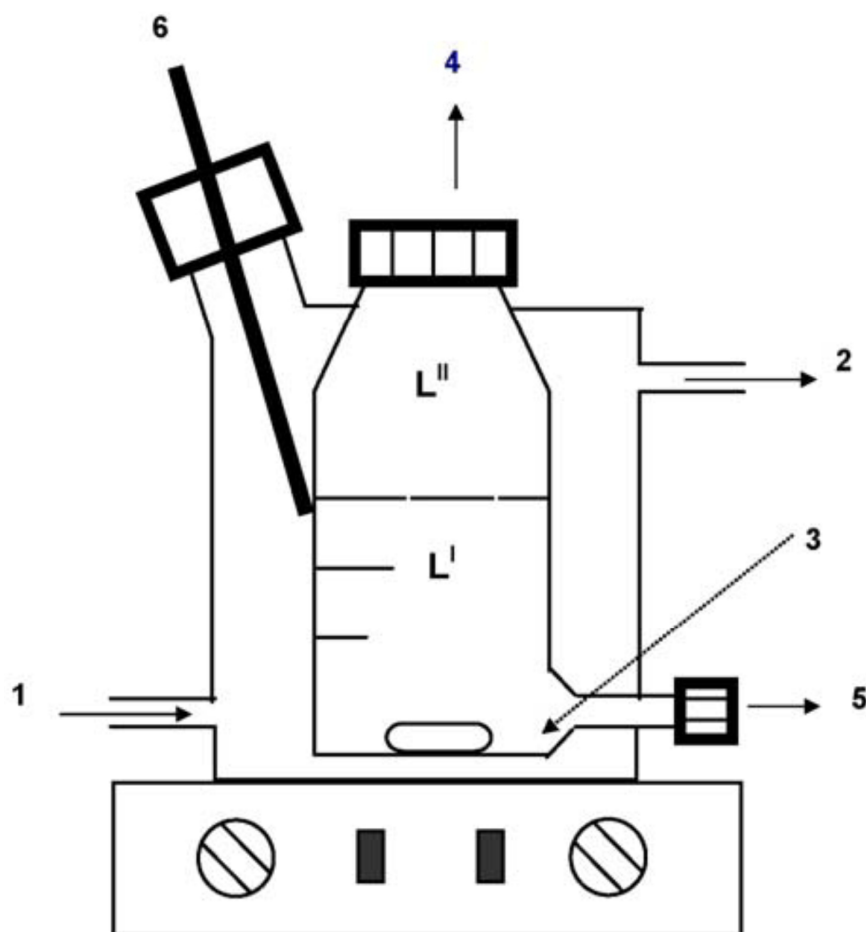


Fig. 1 SCHEMATIC DIAGRAM OF LIQUID-LIQUID EQUILIBRIUM APPARATUS [9]

- (1) Thermostatic water inlet
- (2) Thermostatic water outlet
- (3) Stir bar
- (4) Sampling port for upper phase ( $L^{II}$ )
- (5) Sampling port for lower phase ( $L^I$ )
- (6) Thermometer

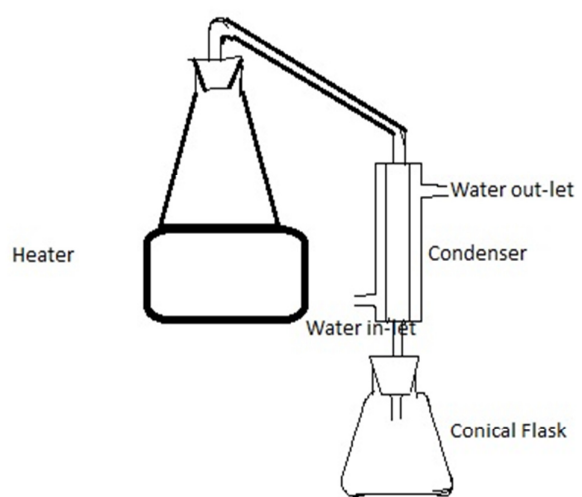


Fig. 2 SCHEMATIC DIAGRAM FOR EVAPORATION OF LIQUID MIXTURE

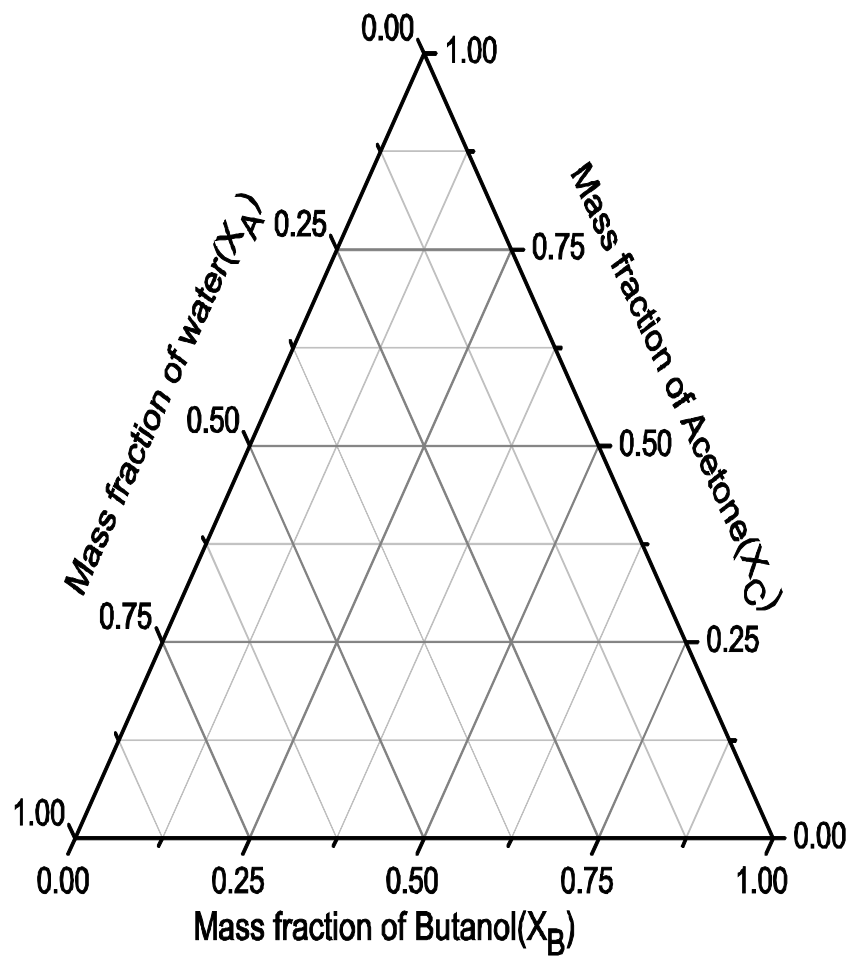


Fig. 3 Triangular Diagram



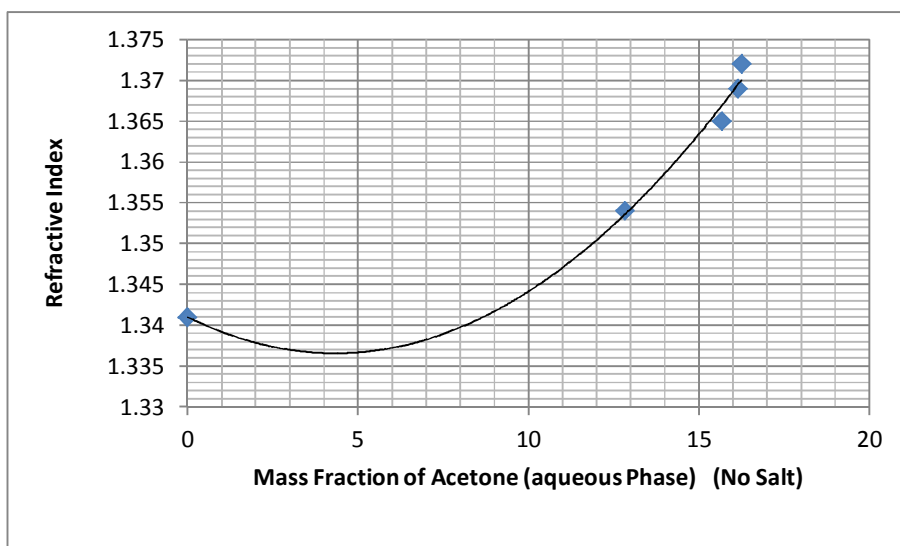


Fig. 4 Mass Fraction vs. Refractive Index (Aqueous Phase) (No Salt)

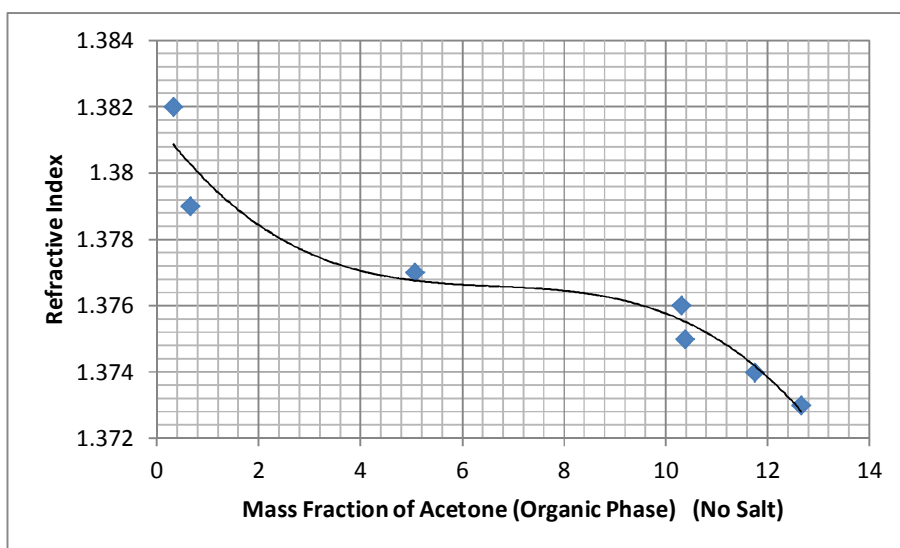


Fig. 5 Mass Fraction vs. Refractive Index (Organic Phase) (No Salt)

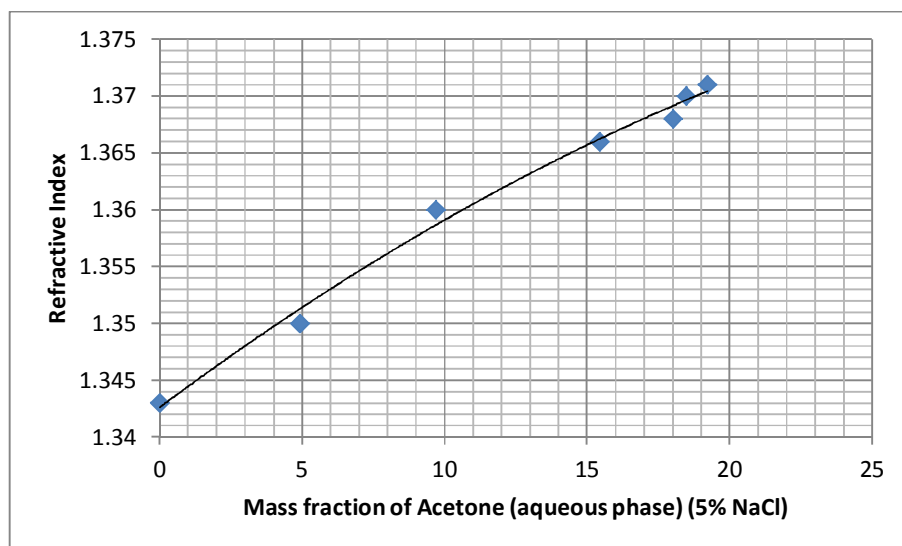


Fig. 6 Mass Fraction vs. Refractive Index (Aqueous Phase) (5% NaCl)

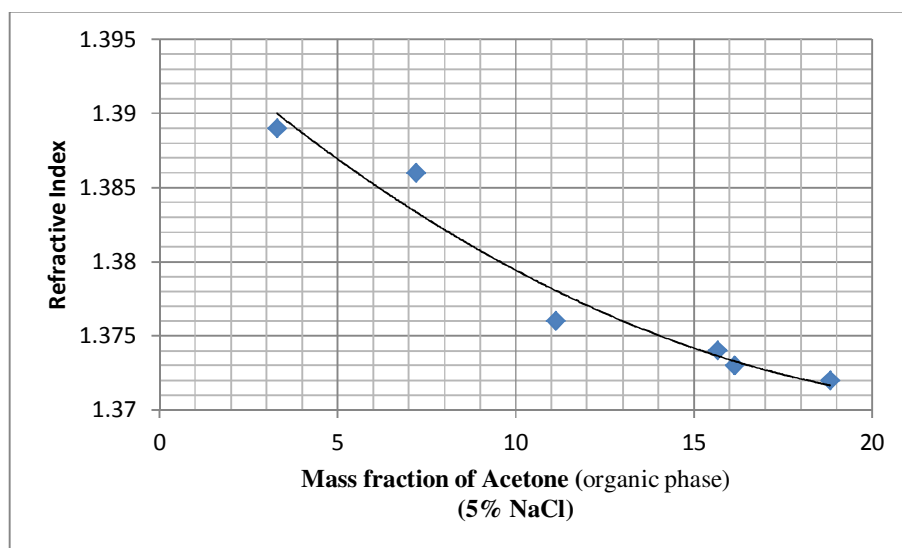


Fig. 7 Mass Fraction vs. Refractive Index (Organic Phase) (5% NaCl)

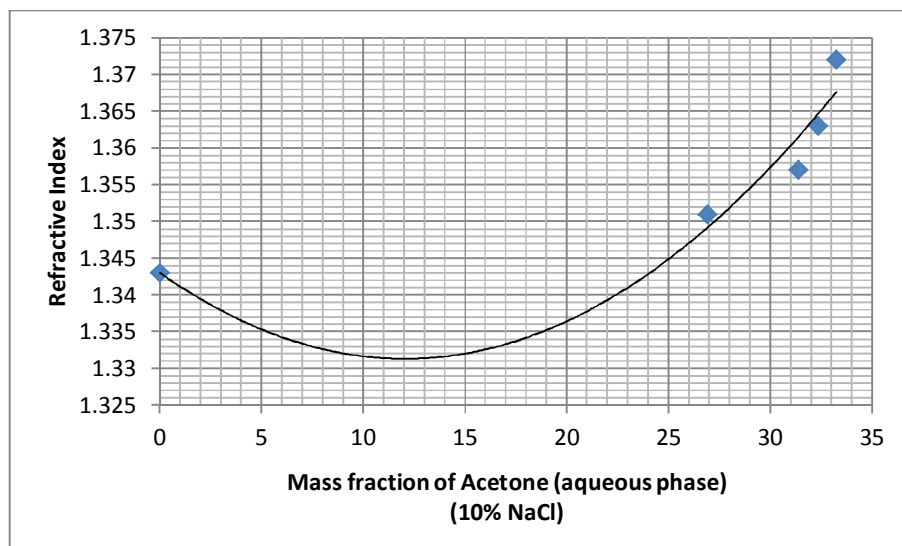


Fig. 8 Mass Fraction vs. Refractive Index (Aqueous Phase) (10% NaCl)

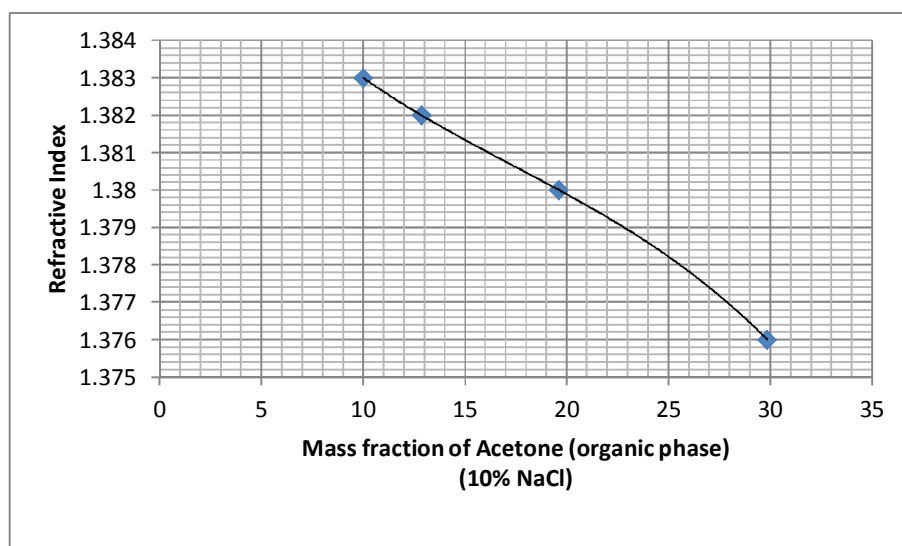


Fig. 9 Mass Fraction vs. Refractive Index (Organic Phase) (10% NaCl)

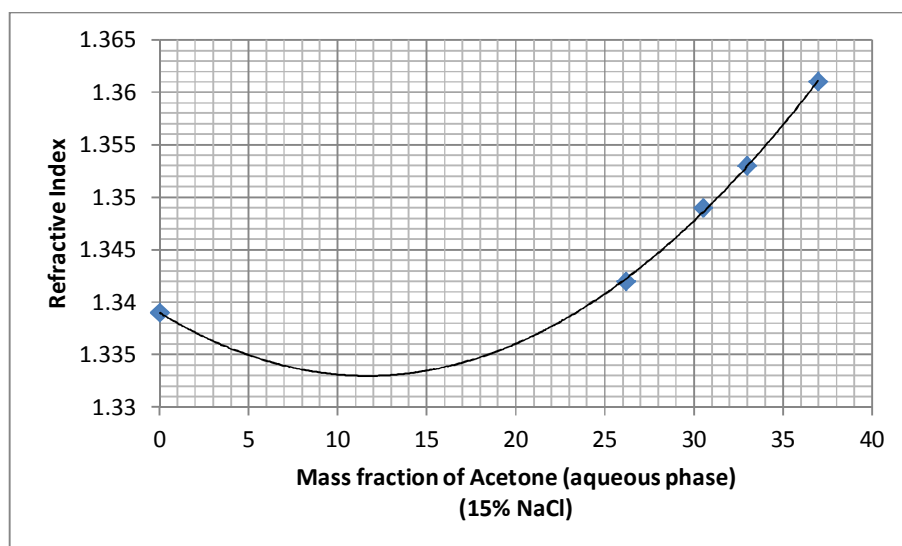


Fig. 10 Mass Fraction vs. Refractive Index (Aqueous Phase) (15% NaCl)

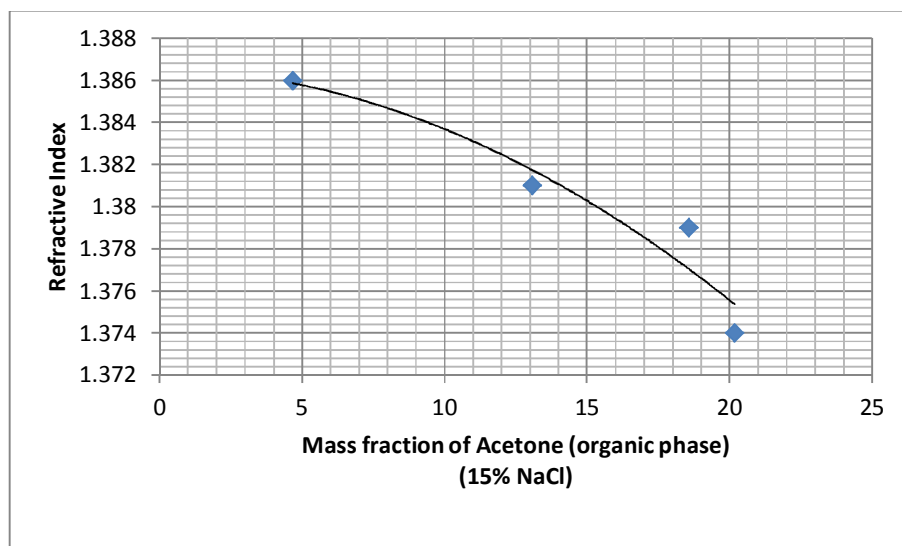


Fig. 11 Mass Fraction vs. Refractive Index (Organic Phase) (15% NaCl)

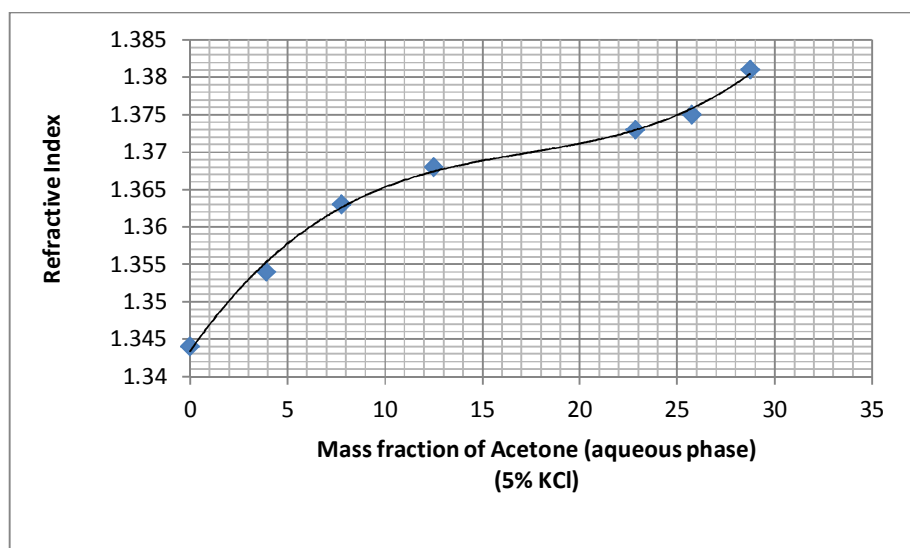


Fig. 12 Mass Fraction vs. Refractive Index (Aqueous Phase) (5% KCl)

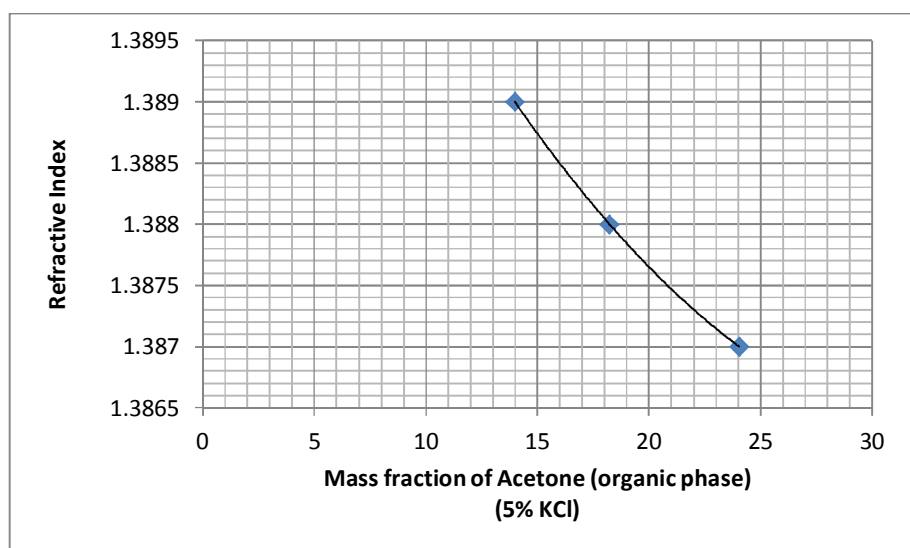


Fig. 13 Mass Fraction vs. Refractive Index (Organic Phase) (5% KCl)

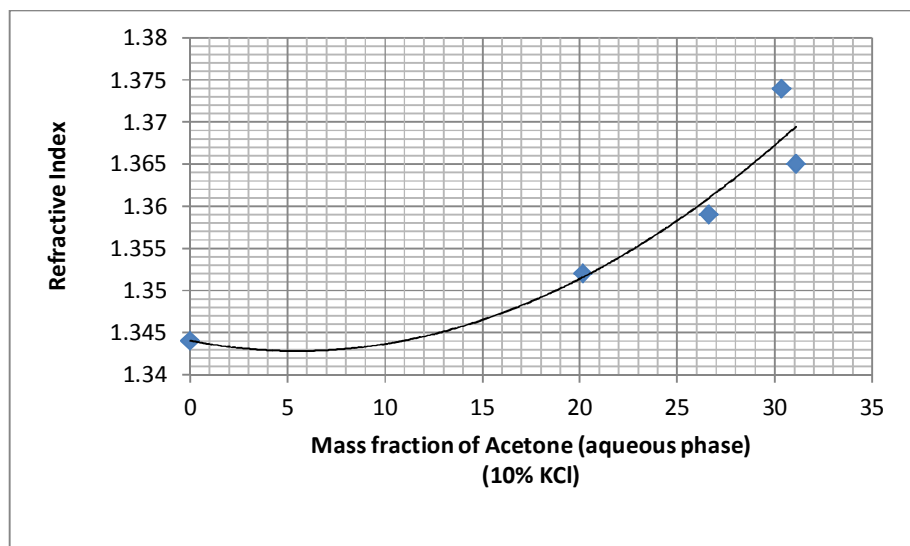


Fig. 14 Mass Fraction vs. Refractive Index (Aqueous Phase) (10% KCl)

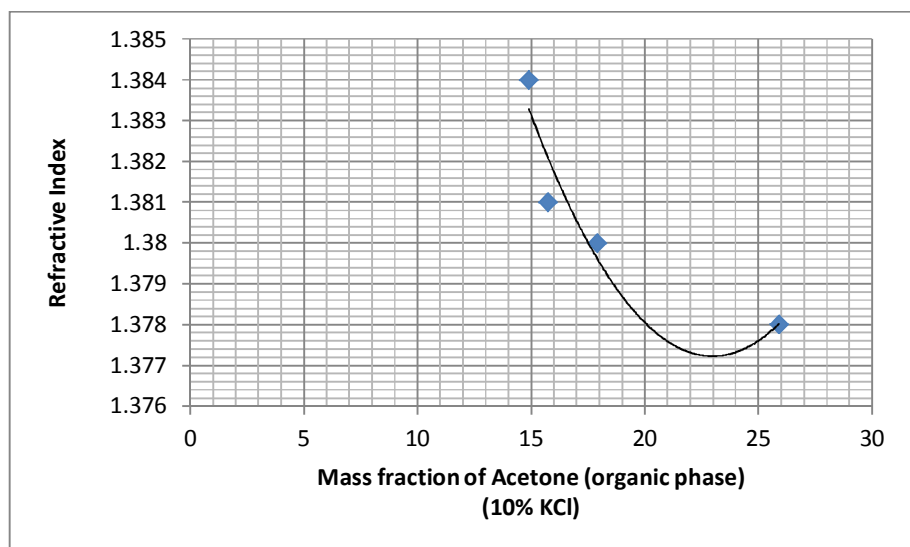


Fig. 15 Mass Fraction vs. Refractive Index (Organic Phase) (10% KCl)

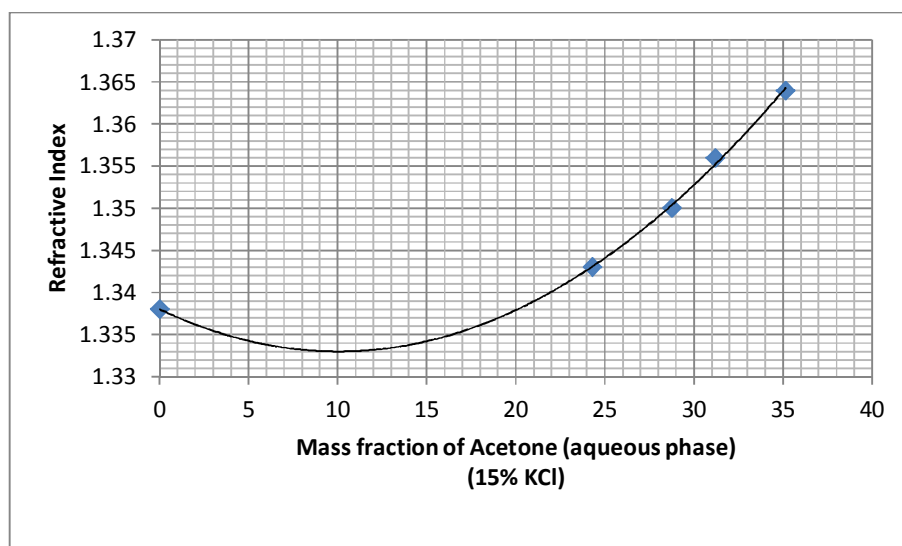


Fig. 16 Mass Fraction vs. Refractive Index (Aqueous Phase) (15% KCl)

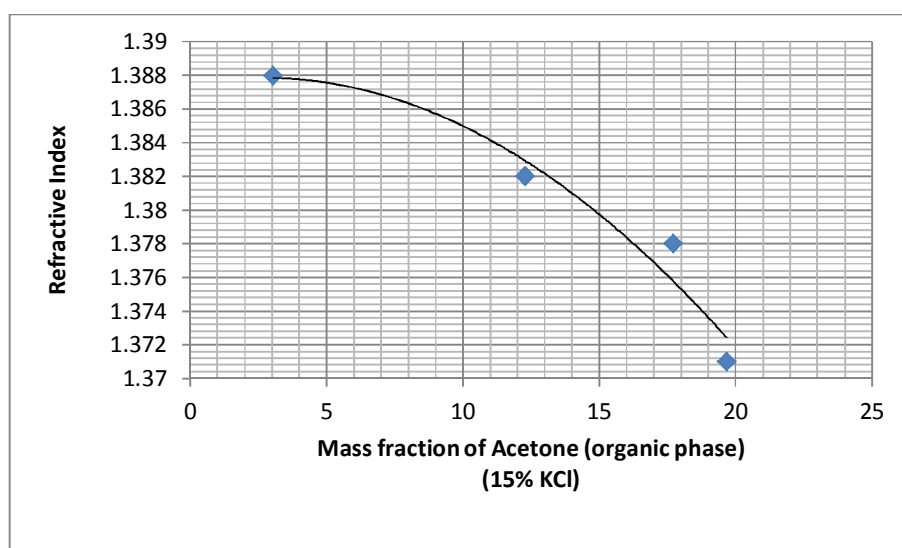


Fig. 17 Mass Fraction vs. Refractive Index (Organic Phase) (15% KCl)

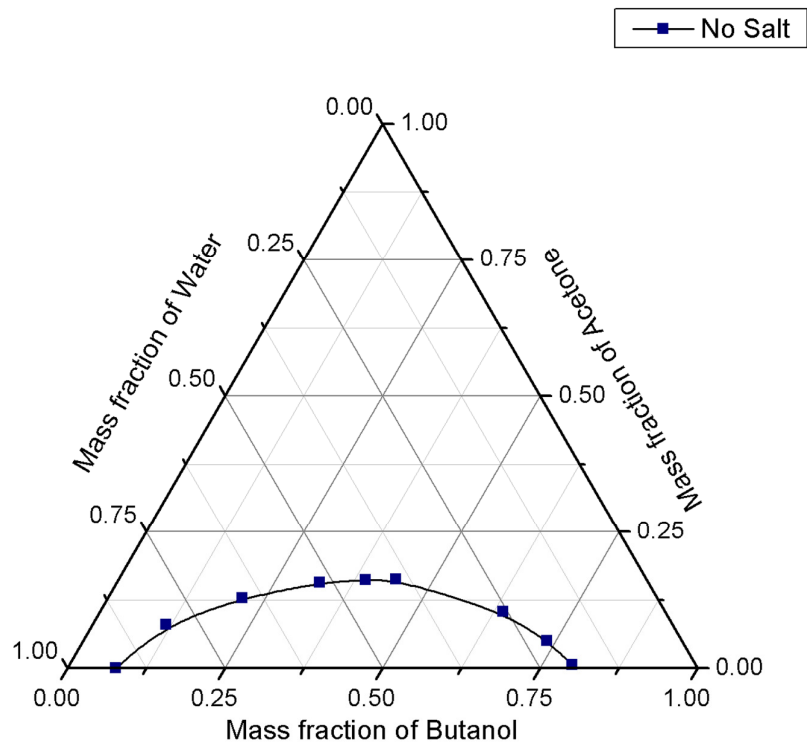


Fig. 18 Solubility curve for no salt



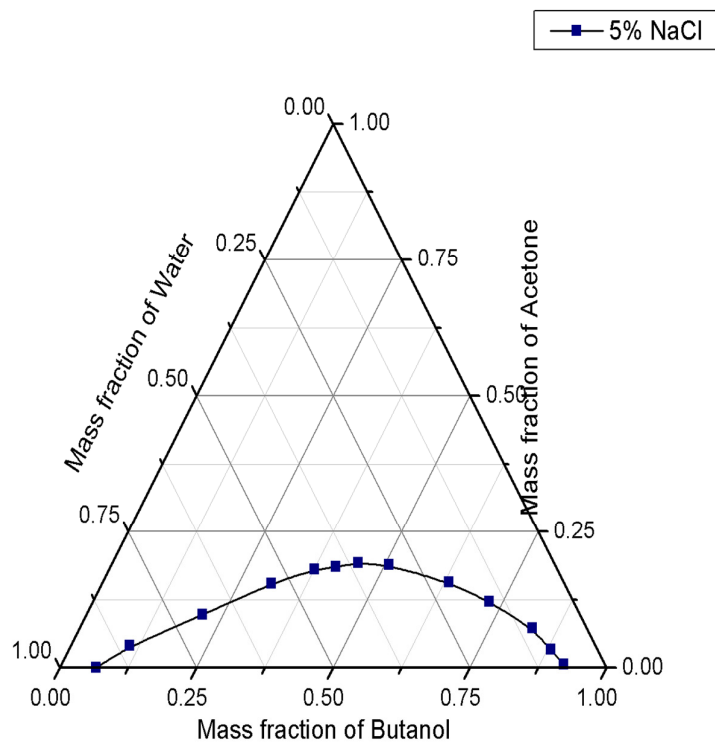


Fig. 19 Solubility curve for 5% NaCl

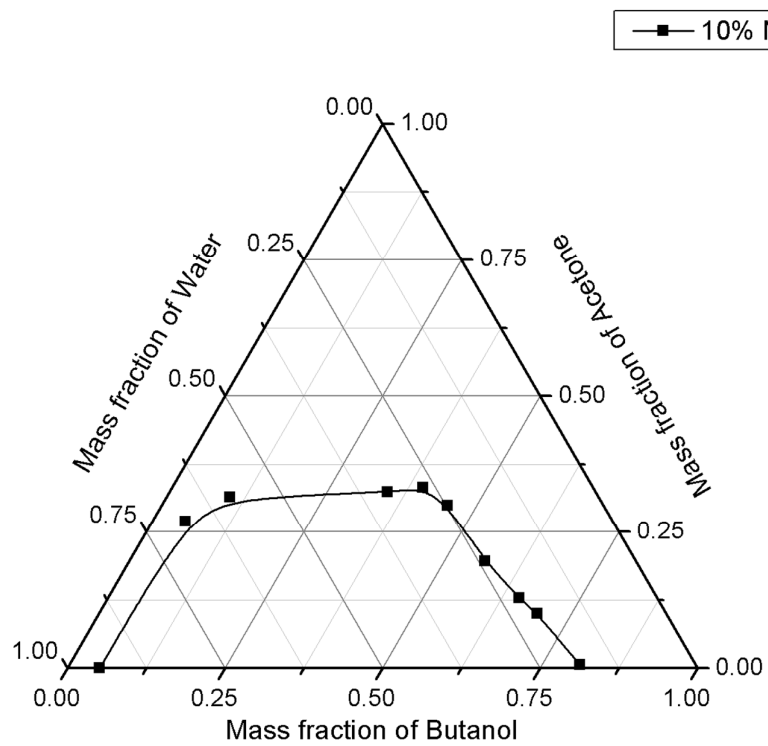


Fig. 20 Solubility curve for 10% NaCl

\

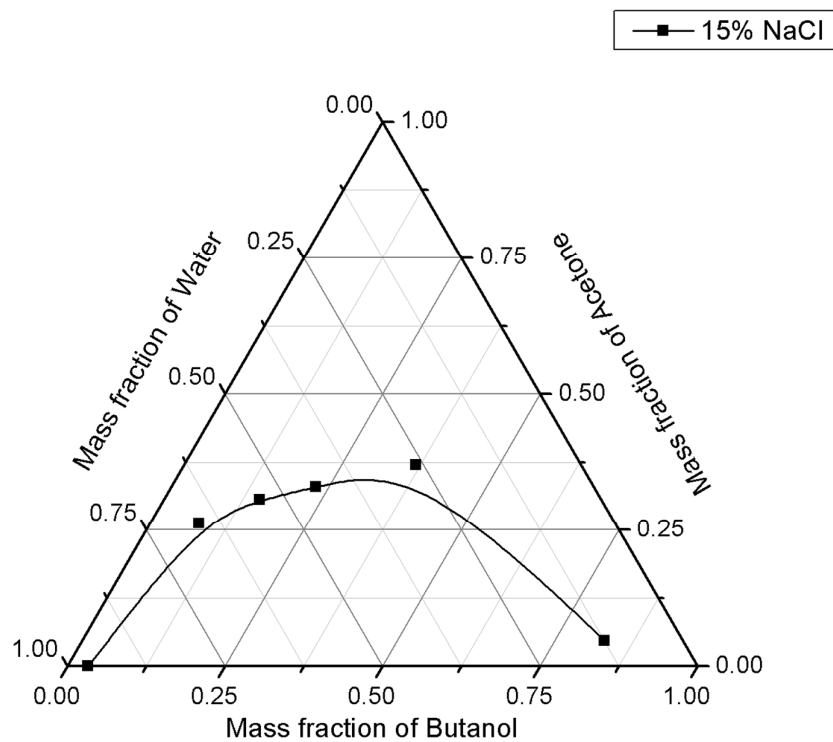


Fig. 21 Solubility Curve for 15% NaCl

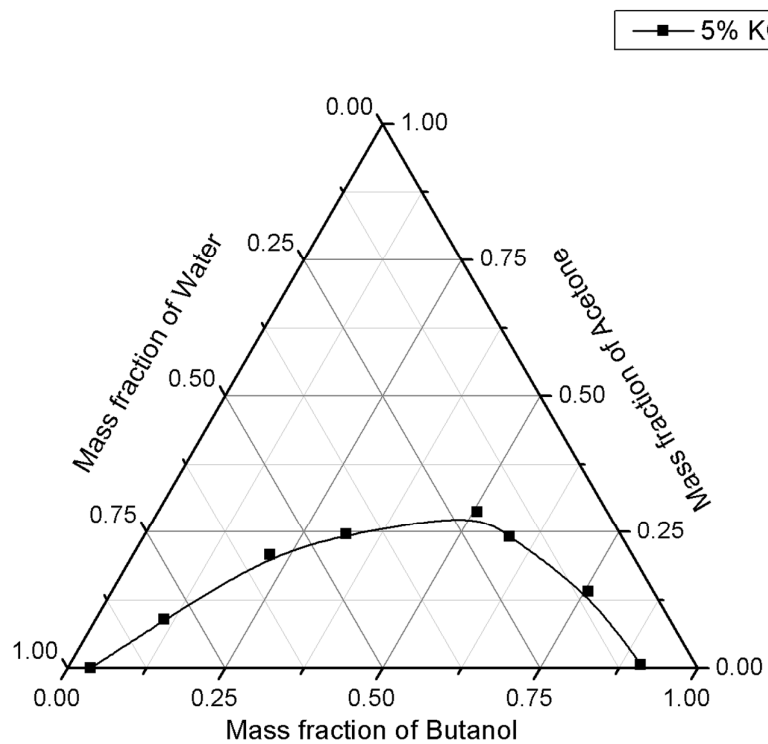


Fig. 22 Solubility curve for 5% KCl

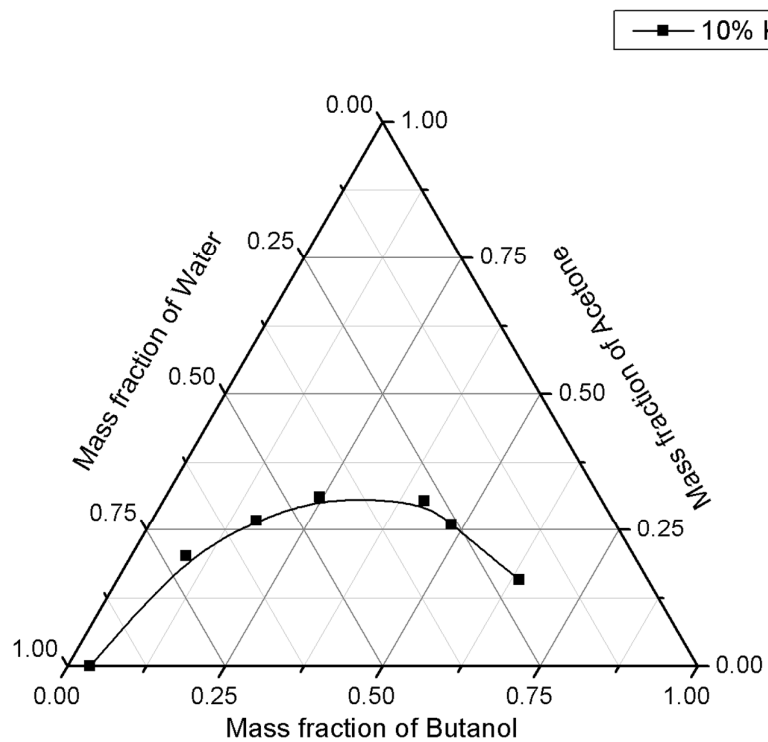


Fig. 23 Solubility Curve for 10% KCl

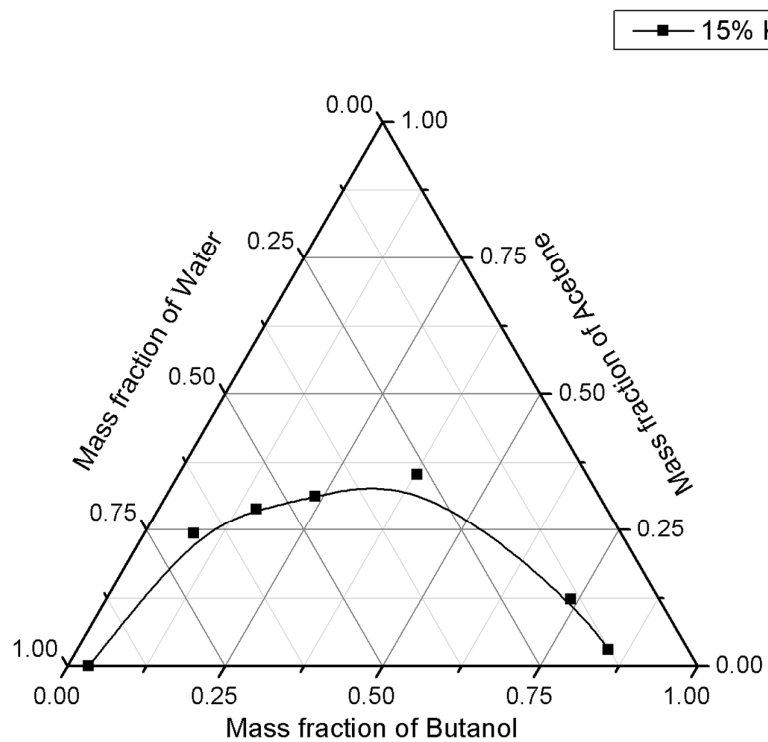


Fig. 24 Solubility Curve for 15% KCl

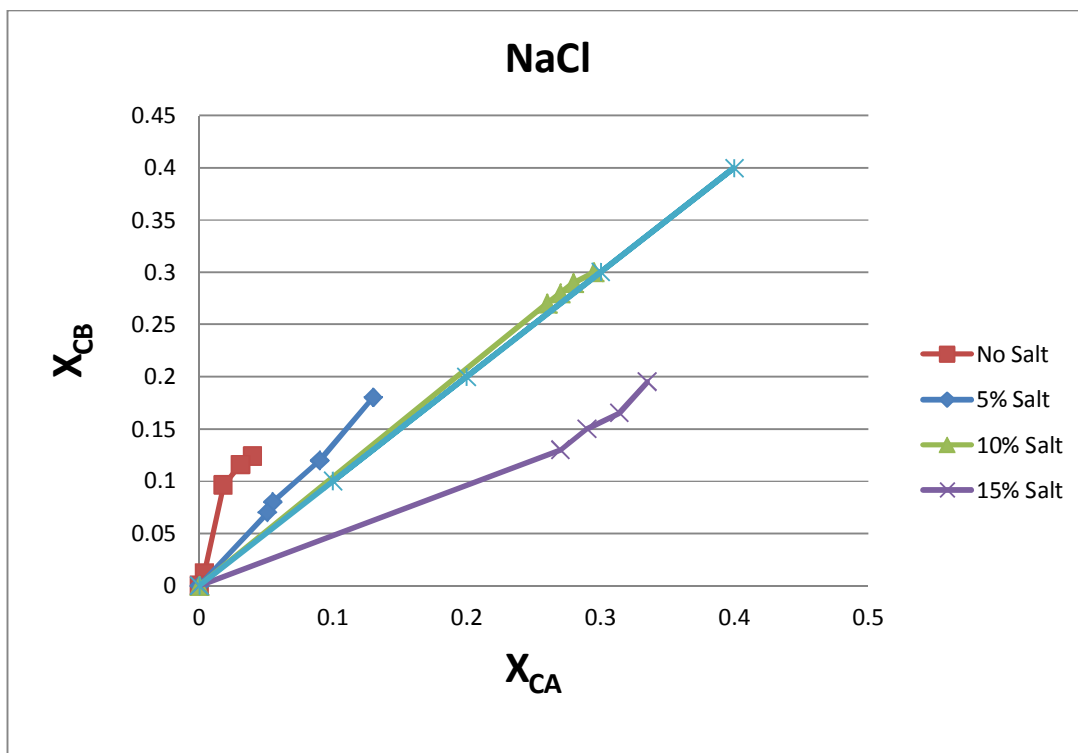


Fig. 25 DISTRIBUTION CURVE

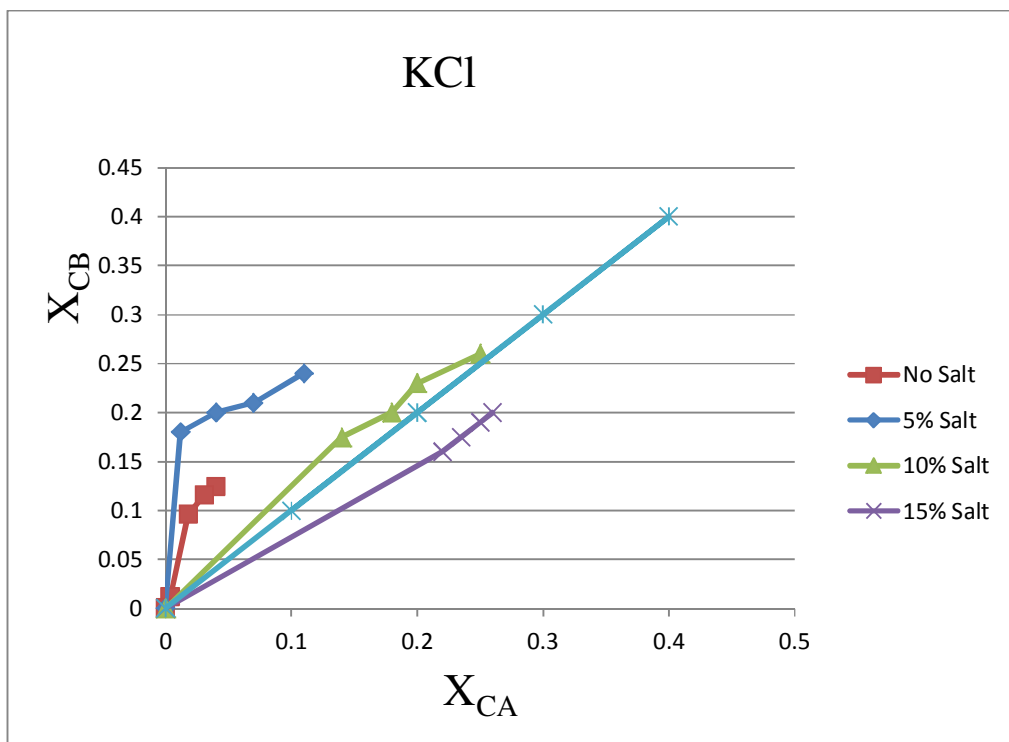


Fig. 26 DISTRIBUTION CURVE

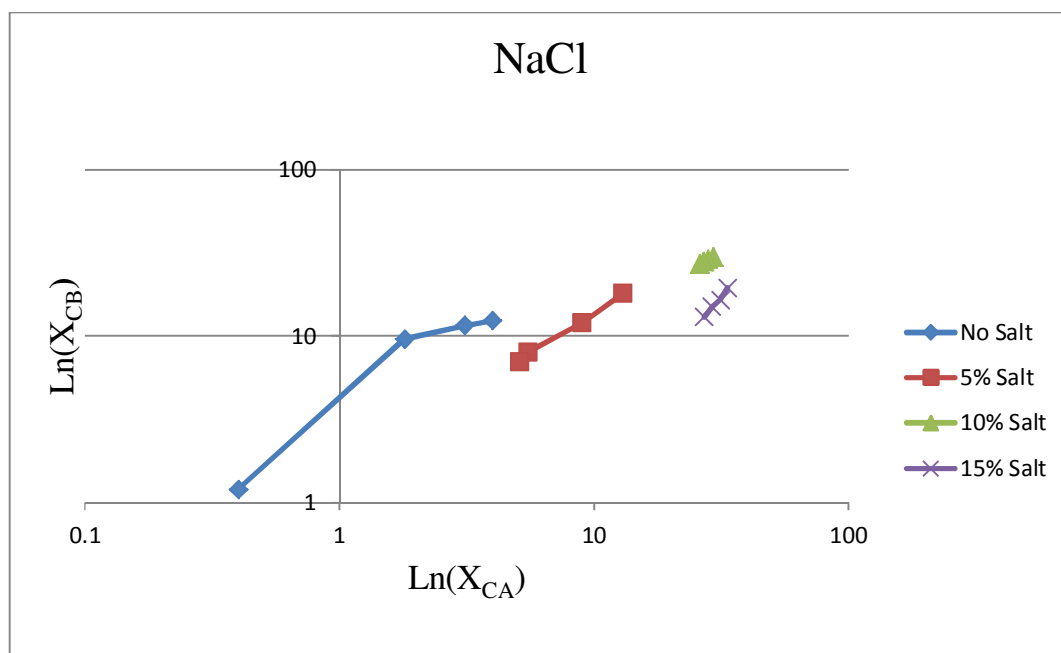


Fig. 27 Campbell's Plot

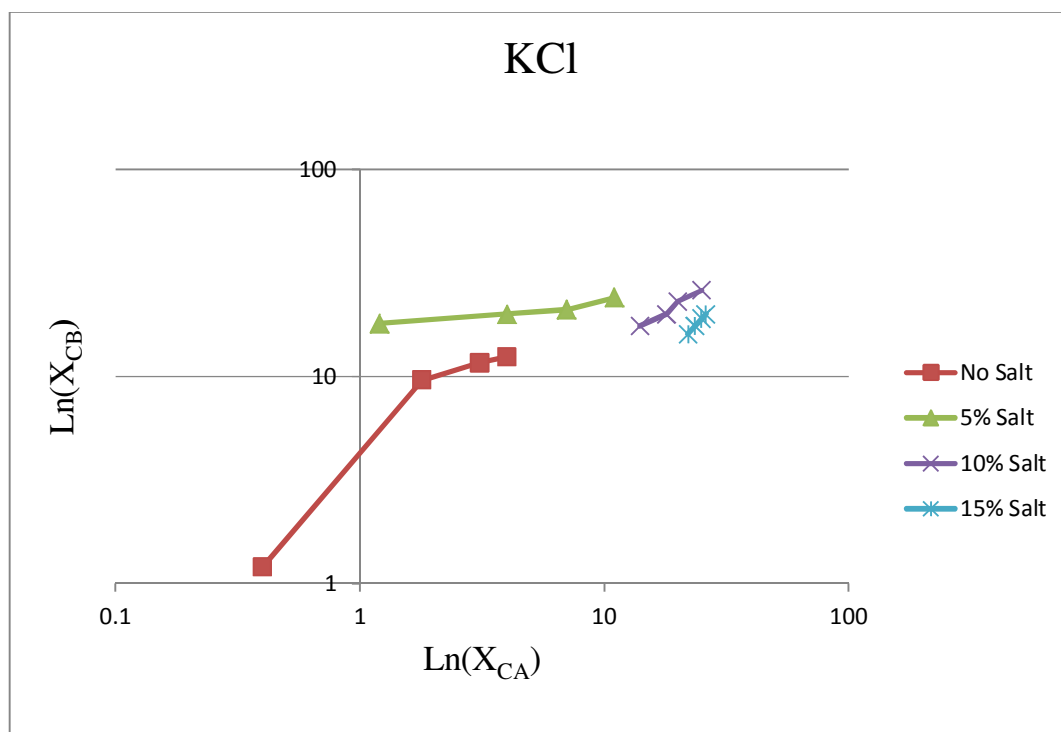


Fig. 28 Campbell's Plot



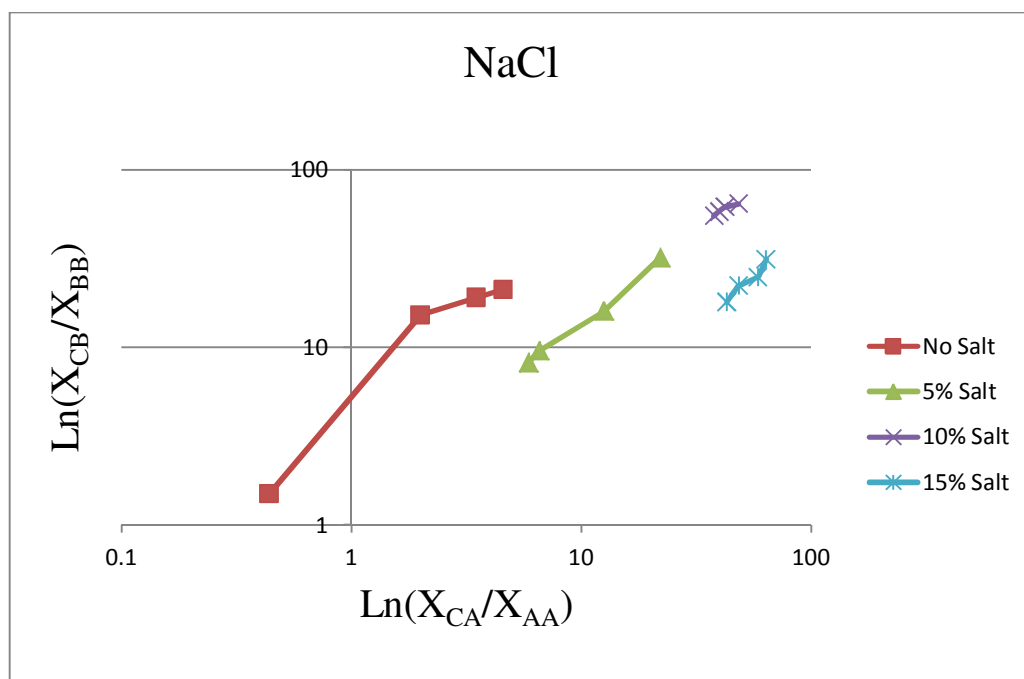


Fig. 29 Hand's Plot

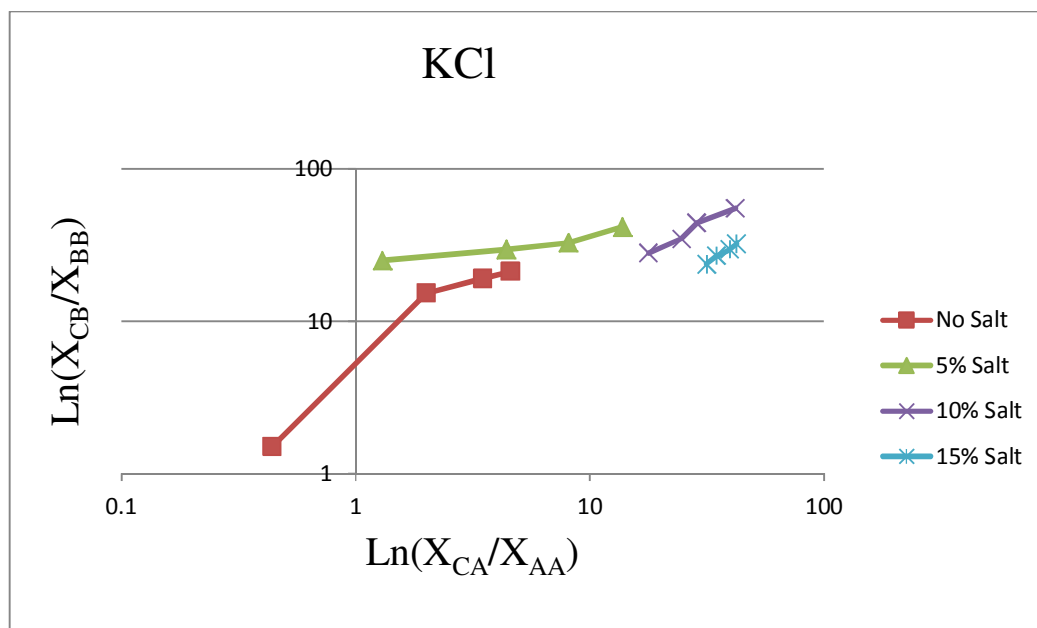


Fig. 30 Hand's Plot

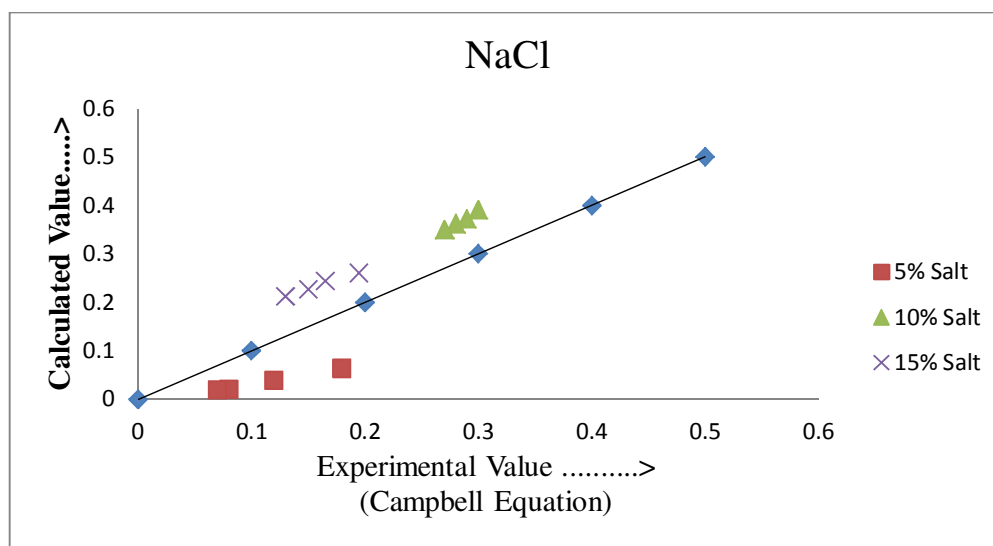


Fig. 31 Experimental vs. Calculated values of mass fraction of acetone (for NaCl)

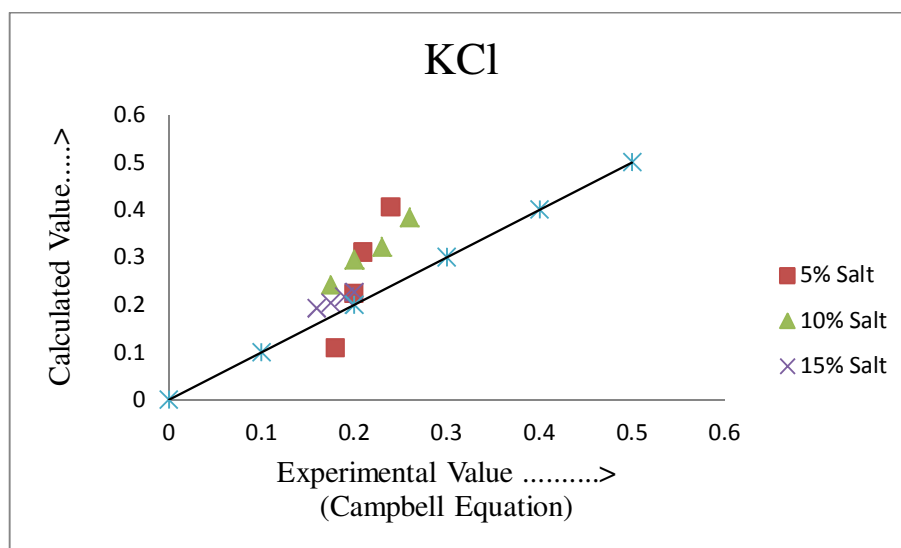


Fig. 32 Experimental vs. Calculated values of mass fraction of acetone (for KCl)

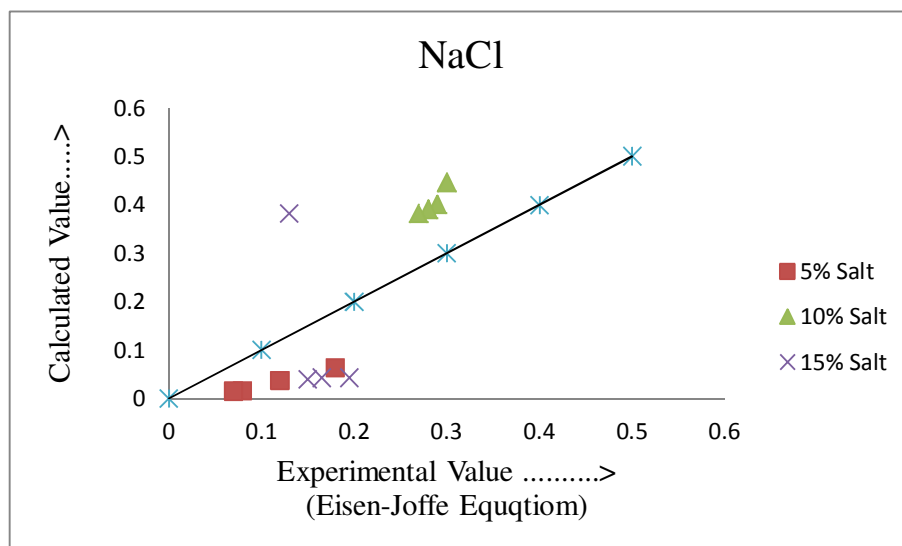


Fig. 33 Experimental vs. Calculated values of mass fraction of acetone (for NaCl)

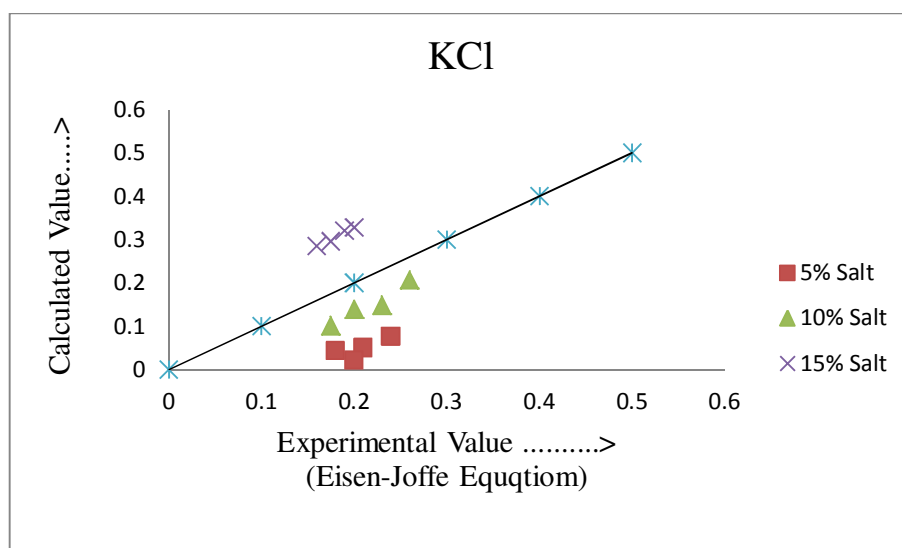


Fig. 34 Experimental vs. Calculated values of mass fraction of acetone (for KCl)

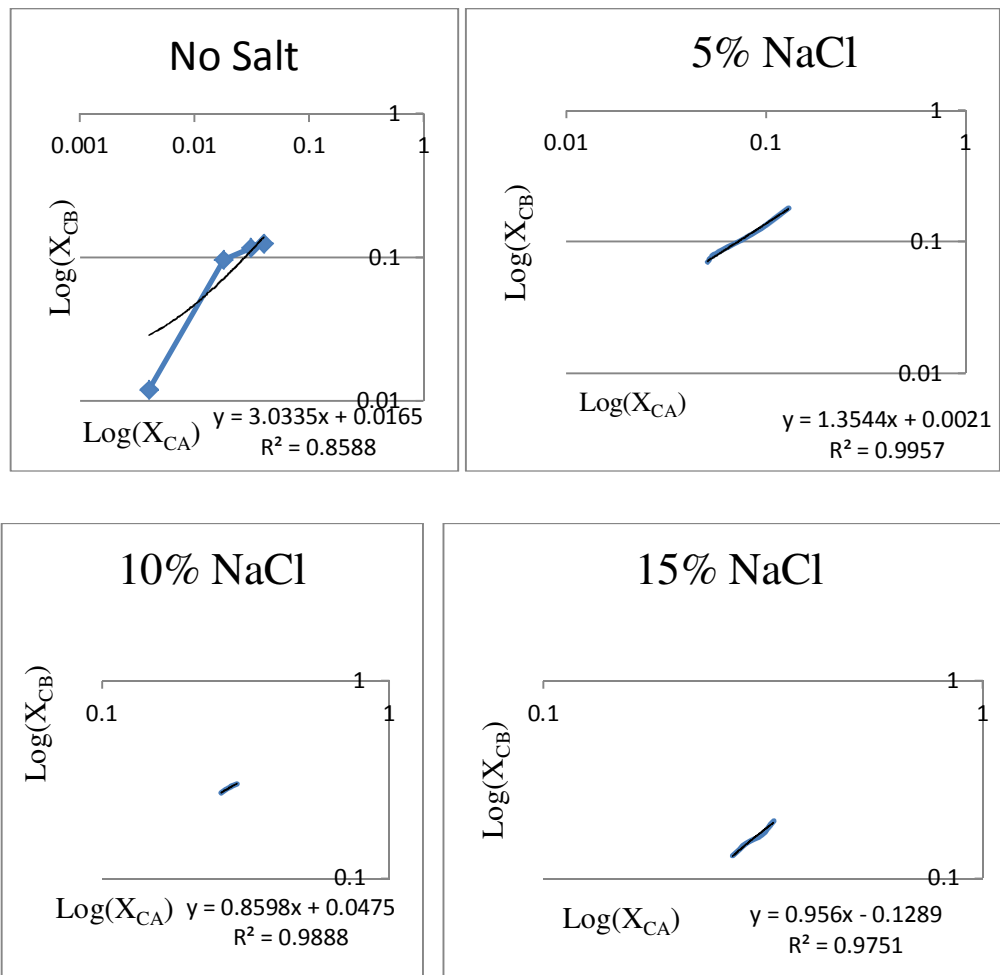


Fig. 35 Determination of Log A & B for NaCl (Campbell Equation)

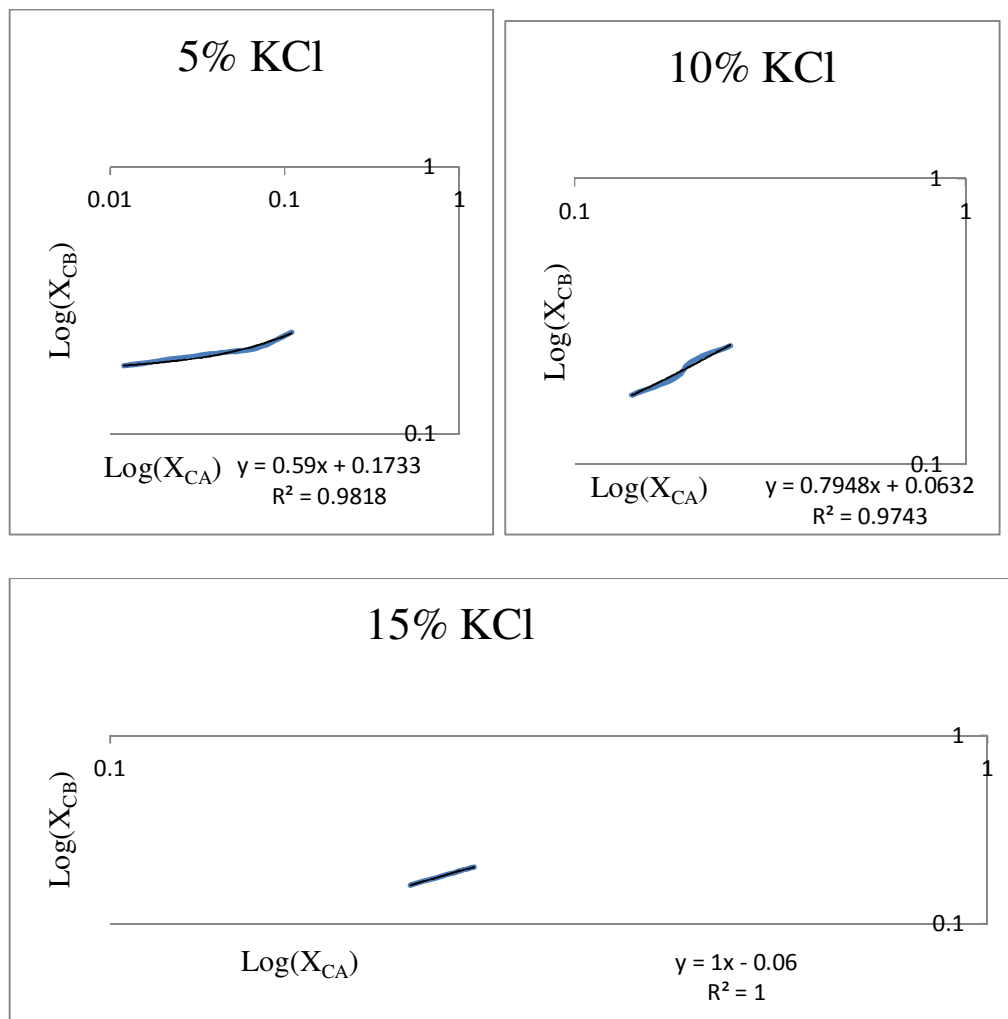


Fig. 36 Determination of Log A & B for KCl (Campbell Equation)

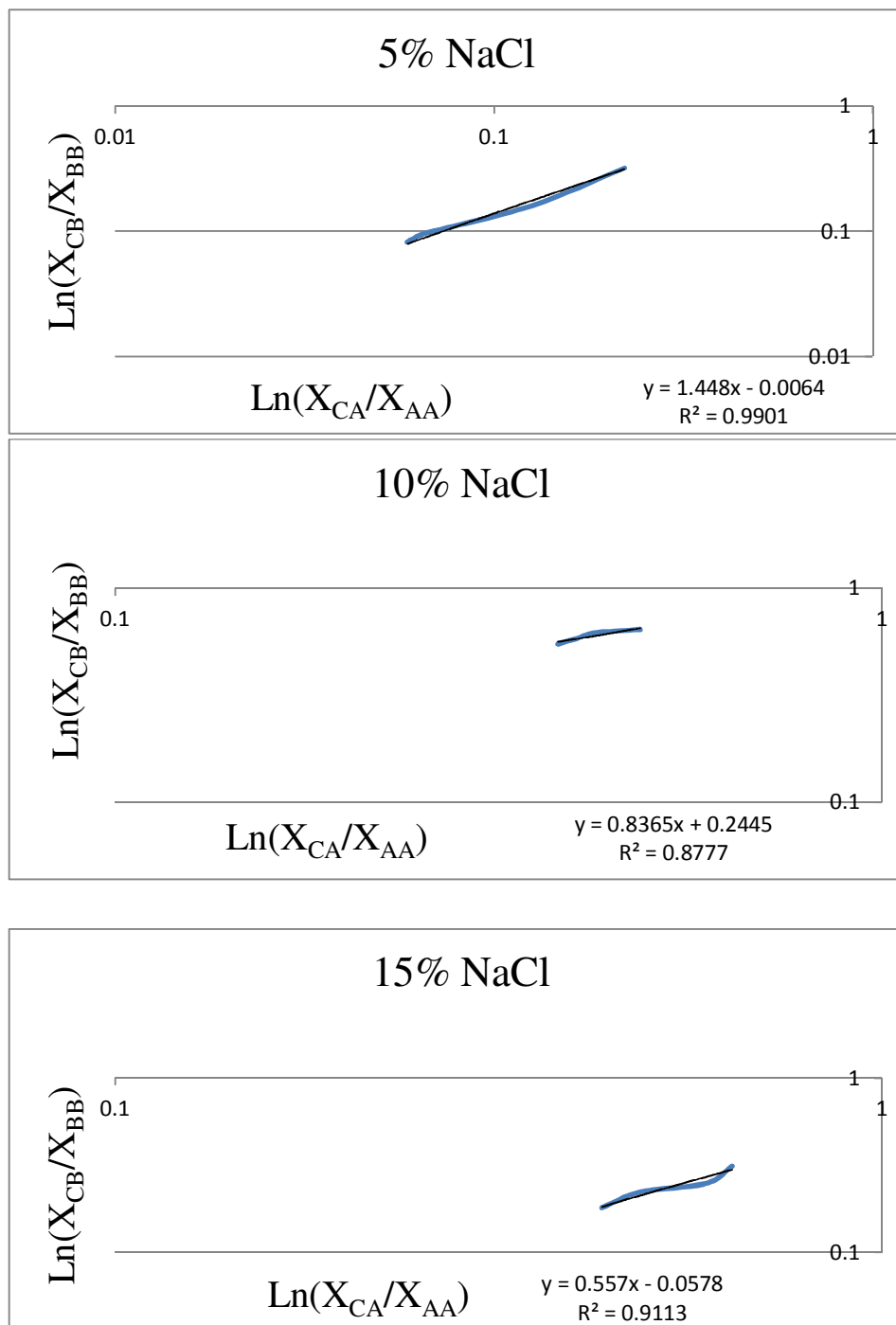


Fig. 37 Determination of Log A & B for NaCl(Hand's Equation)

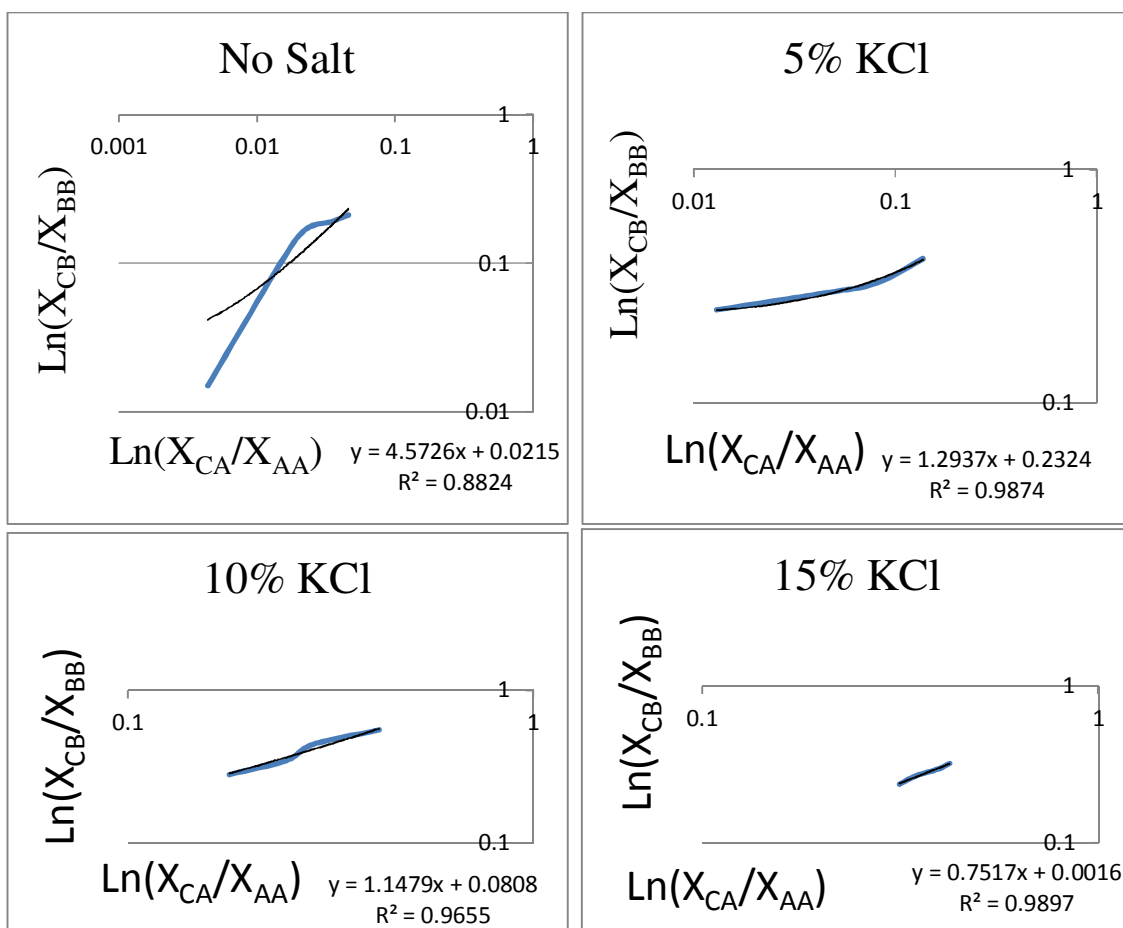


Fig. 38 Determination of Log A & B for KCl(Hand's Equation)

TABLE – 4.1  
SOLUBILITY DATA  
(For All Systems)

System: Water + Acetone + 1-Butanol

Table 4.1.1

1. NO SALT

| SL.No | X <sub>A</sub> | X <sub>B</sub> | X <sub>C</sub> | Refractive Index |
|-------|----------------|----------------|----------------|------------------|
| 1     | 92.53          | 7.65           | 0              | 1.341            |
| 2     | 80.67          | 11.62          | 18.71          | 1.348            |
| 3     | 65.84          | 21.33          | 12.83          | 1.354            |
| 4     | 52.08          | 32.25          | 15.67          | 1.365            |
| 5     | 44.52          | 39.34          | 16.14          | 1.369            |
| 6     | 39.67          | 44.09          | 16.24          | 1.372            |
| 7     | 37.71          | 49.63          | 12.66          | 1.373            |
| 8     | 33.92          | 54.33          | 11.75          | 1.374            |
| 9     | 30.64          | 58.98          | 10.38          | 1.375            |
| 10    | 25.69          | 64.0           | 10.31          | 1.376            |
| 11    | 21.38          | 73.56          | 5.06           | 1.377            |
| 12    | 19.53          | 79.82          | 0.65           | 1.379            |
| 13    | 16.47          | 83.21          | 0.32           | 1.382            |

Table 4.1.2 (i)

2. SALT: SODIUM CHLORIDE (NaCl)

(i) 5% By Weight

| SL. No | X <sub>A</sub> | X <sub>B</sub> | X <sub>C</sub> | Refractive Index |
|--------|----------------|----------------|----------------|------------------|
| 1      | 93.65          | 6.65           | 0              | 1.343            |
| 2      | 85.24          | 10.83          | 4.03           | 1.350            |
| 3      | 69.01          | 21.3           | 9.69           | 1.360            |
| 4      | 53.56          | 30.99          | 15.45          | 1.366            |
| 5      | 44.35          | 37.63          | 18.02          | 1.368            |
| 6      | 40.19          | 41.33          | 18.48          | 1.370            |
| 7      | 35.85          | 44.93          | 19.22          | 1.371            |
| 8      | 30.35          | 50.82          | 18.83          | 1.372            |
| 9      | 28.88          | 54.98          | 16.14          | 1.373            |
| 10     | 21.0           | 63.33          | 15.67          | 1.374            |
| 11     | 15.33          | 72.55          | 12.12          | 1.376            |
| 12     | 9.94           | 82.86          | 7.20           | 1.386            |
| 13     | 8.45           | 88.25          | 3.3            | 1.389            |



Table 4.1.2 (ii)

(ii) 10% By Weight

| SL.No | X <sub>A</sub> | X <sub>B</sub> | X <sub>C</sub> | Refractive Index |
|-------|----------------|----------------|----------------|------------------|
| 1     | 94.9           | 5.10           | 0              | 1.343            |
| 2     | 67.82          | 5.26           | 26.91          | 1.351            |
| 3     | 58.49          | 10.14          | 31.37          | 1.357            |
| 4     | 33.02          | 34.63          | 32.35          | 1.363            |
| 5     | 26.99          | 39.76          | 33.24          | 1.372            |
| 6     | 24.7           | 45.46          | 29.85          | 1.376            |
| 7     | 23.95          | 56.44          | 19.61          | 1.380            |
| 8     | 21.84          | 65.3           | 12.86          | 1.382            |
| 9     | 20.44          | 69.56          | 10.0           | 1.383            |

Table 4.1.2 (iii)

(iii) 15% By Weight

| SL. No | X <sub>A</sub> | X <sub>B</sub> | X <sub>C</sub> | Refractive Index |
|--------|----------------|----------------|----------------|------------------|
| 1      | 96.7           | 3.3            | 0              | 1.339            |
| 2      | 66.04          | 7.75           | 26.21          | 1.342            |
| 3      | 54.2           | 15.27          | 30.53          | 1.349            |
| 4      | 44.0           | 23.0           | 33.0           | 1.353            |
| 5      | 26.16          | 36.86          | 36.98          | 1.361            |
| 6      | 28.91          | 51.0           | 20.18          | 1.374            |
| 7      | 25.03          | 56.41          | 18.56          | 1.379            |
| 8      | 21.76          | 65.15          | 13.08          | 1.381            |
| 9      | 12.39          | 82.92          | 4.68           | 1.386            |

Table 4.1.3 (i)

3. SALT: POTASSIUM CHLORIDE (KCl)

(i) 5% By Weight

| SL. No | X <sub>A</sub> | X <sub>B</sub> | X <sub>C</sub> | Refractive Index |
|--------|----------------|----------------|----------------|------------------|
| 1      | 96.3           | 3.7            | 0              | 1.344            |
| 2      | 80.14          | 10.95          | 8.91           | 1.354            |
| 3      | 57.48          | 21.75          | 20.77          | 1.363            |
| 4      | 43.42          | 32.07          | 24.51          | 1.368            |
| 5      | 30.35          | 46.82          | 22.83          | 1.373            |
| 6      | 25.35          | 48.89          | 25.75          | 1.375            |
| 7      | 20.54          | 50.71          | 28.74          | 1.381            |
| 8      | 17.75          | 58.20          | 24.04          | 1.387            |
| 9      | 10.33          | 75.69          | 13.98          | 1.389            |

Table 4.1.3 (ii)

(ii) 10% By Weight

| SL. No | X <sub>A</sub> | X <sub>B</sub> | X <sub>C</sub> | Refractive Index |
|--------|----------------|----------------|----------------|------------------|
| 1      | 96.45          | 3.55           | 0              | 1.344            |
| 2      | 71.12          | 8.73           | 20.15          | 1.352            |
| 3      | 56.69          | 16.69          | 26.62          | 1.359            |
| 4      | 44.39          | 24.51          | 31.1           | 1.365            |
| 5      | 28.16          | 41.48          | 30.36          | 1.374            |
| 6      | 26.08          | 48.01          | 25.91          | 1.378            |
| 7      | 24.46          | 57.63          | 17.91          | 1.380            |
| 8      | 20.40          | 63.85          | 15.75          | 1.381            |
| 9      | 10.64          | 74.45          | 14.9           | 1.384            |

Table 4.1.3 (iii)

(iii) 15% By Weight

| SL. No | X <sub>A</sub> | X <sub>B</sub> | X <sub>C</sub> | Refractive Index |
|--------|----------------|----------------|----------------|------------------|
| 1      | 96.6           | 3.4            | 0              | 1.338            |
| 2      | 67.74          | 7.95           | 24.31          | 1.343            |
| 3      | 55.57          | 15.65          | 28.78          | 1.350            |
| 4      | 45.03          | 23.78          | 31.19          | 1.356            |
| 5      | 26.92          | 37.93          | 35.15          | 1.364            |
| 6      | 29.10          | 51.24          | 19.66          | 1.371            |
| 7      | 25.30          | 57.0           | 17.7           | 1.378            |
| 8      | 13.93          | 73.79          | 12.28          | 1.382            |
| 9      | 12.61          | 84.36          | 3.03           | 1.388            |

TABLE – 4.2  
EQUILIBRIUM DATA  
(For All Systems)

System: Water + Acetone + 1-Butanol

TABLE -4.2.1

1. NO SALT

| Water Layer |          |          |          |                  |
|-------------|----------|----------|----------|------------------|
| SL. No.     | $X_{AA}$ | $X_{BA}$ | $X_{CA}$ | Refractive Index |
| 1           | 0.86     | 0.11     | 0.13     | 1.354            |
| 2           | 0.882    | 0.099    | 0.125    | 1.352            |
| 3           | 0.893    | 0.089    | 0.108    | 1.347            |
| 4           | 0.915    | 0.081    | 0.09     | 1.342            |

| Butanol Layer |          |          |          |                  |
|---------------|----------|----------|----------|------------------|
| SL. No.       | $X_{AB}$ | $X_{BB}$ | $X_{CB}$ | Refractive Index |
| 1             | 0.305    | 0.588    | 0.124    | 1.3728           |
| 2             | 0.272    | 0.61     | 0.116    | 1.374            |
| 3             | 0.261    | 0.632    | 0.096    | 1.376            |
| 4             | 0.198    | 0.775    | 0.012    | 1.379            |

TABLE -4.2.2(i)

2. SODIUM CHLORIDE (NaCl)

(i) 5% By weight

| Water Layer |          |          |          |           |                  |
|-------------|----------|----------|----------|-----------|------------------|
| SL. No.     | $X_{AA}$ | $X_{BA}$ | $X_{CA}$ | %Wt. Salt | Refractive index |
| 1           | 0.588    | 0.275    | 0.13     | 3.21      | 1.363            |
| 2           | 0.709    | 0.187    | 0.09     | 3.92      | 1.358            |
| 3           | 0.827    | 0.125    | 0.055    | 4.08      | 1.354            |
| 4           | 0.851    | 0.1083   | 0.051    | 4.5       | 1.352            |

| Butanol Layer |                 |                 |                 |           |                  |
|---------------|-----------------|-----------------|-----------------|-----------|------------------|
| SL. No.       | X <sub>AB</sub> | X <sub>BB</sub> | X <sub>CB</sub> | %Wt. Salt | Refractive Index |
| 1             | 0.261           | 0.566           | 0.18            | 1.69      | 1.372            |
| 2             | 0.143           | 0.75            | 0.12            | 1.22      | 1.377            |
| 3             | 0.11            | 0.827           | 0.08            | 0.61      | 1.382            |
| 4             | 0.099           | 0.849           | 0.07            | 0.60      | 1.384            |

TABLE -4.2.2(ii)  
(ii) 10% By weight

| Water Layer |                 |                 |                 |           |                  |
|-------------|-----------------|-----------------|-----------------|-----------|------------------|
| SL. No.     | X <sub>AA</sub> | X <sub>BA</sub> | X <sub>CA</sub> | %Wt. Salt | Refractive index |
| 1           | 0.61            | 0.088           | 0.295           | 5.94      | 1.356            |
| 2           | 0.663           | 0.05            | 0.28            | 6.33      | 1.352            |
| 3           | 0.676           | 0.077           | 0.27            | 7.56      | 1.349            |
| 4           | 0.687           | 0.053           | 0.26            | 8.2       | 1.348            |

| Butanol Layer |                 |                 |                 |           |                  |
|---------------|-----------------|-----------------|-----------------|-----------|------------------|
| SL. No.       | X <sub>AB</sub> | X <sub>BB</sub> | X <sub>CB</sub> | %Wt. Salt | Refractive Index |
| 1             | 0.244           | 0.468           | 0.3             | 4.19      | 1.376            |
| 2             | 0.24            | 0.47            | 0.29            | 3.62      | 1.3764           |
| 3             | 0.239           | 0.481           | 0.28            | 2.31      | 1.377            |
| 4             | 0.22            | 0.492           | 0.27            | 1.8       | 1.3774           |

TABLE -4.2.2(iii)  
(iii) 15% By weight

| Water Layer |                 |                 |                 |           |                  |
|-------------|-----------------|-----------------|-----------------|-----------|------------------|
| SL. No.     | X <sub>AA</sub> | X <sub>BA</sub> | X <sub>CA</sub> | %Wt. Salt | Refractive index |
| 1           | 0.525           | 0.158           | 0.335           | 9.21      | 1.354            |
| 2           | 0.533           | 0.153           | 0.314           | 11.02     | 1.350            |
| 3           | 0.599           | 0.111           | 0.29            | 11.54     | 1.346            |
| 4           | 0.6265          | 0.1035          | 0.27            | 13.4      | 1.343            |

| Butanol Layer |                 |                 |                 |           |                  |
|---------------|-----------------|-----------------|-----------------|-----------|------------------|
| SL. No.       | X <sub>AB</sub> | X <sub>BB</sub> | X <sub>CB</sub> | %Wt. Salt | Refractive Index |
| 1             | 0.18            | 0.625           | 0.195           | 5.79      | 1.376            |
| 2             | 0.17            | 0.665           | 0.165           | 4.0       | 1.378            |
| 3             | 0.168           | 0.675           | 0.15            | 3.26      | 1.380            |
| 4             | 0.163           | 0.698           | 0.13            | 1.25      | 1.382            |

TABLE -4.2.3 (i)

### 3. SALT: POTASSIUM CHLORIDE (KCL)

(i) 5% By weight

| Water Layer |                 |                 |                 |           |                  |
|-------------|-----------------|-----------------|-----------------|-----------|------------------|
| SL. No.     | X <sub>AA</sub> | X <sub>BA</sub> | X <sub>CA</sub> | %Wt. Salt | Refractive index |
| 1           | 0.80            | 0.09            | 0.11            | 3.15      | 1.366            |
| 2           | 0.8625          | 0.0625          | 0.07            | 3.3       | 1.362            |
| 3           | 0.9125          | 0.05            | 0.04            | 3.5       | 1.356            |
| 4           | 0.915           | 0.041           | 0.012           | 4.32      | 1.348            |

| Butanol Layer |                 |                 |                 |           |                  |
|---------------|-----------------|-----------------|-----------------|-----------|------------------|
| SL. No.       | X <sub>AB</sub> | X <sub>BB</sub> | X <sub>CB</sub> | %Wt. Salt | Refractive Index |
| 1             | 0.183           | 0.577           | 0.24            | 1.55      | 1.387            |
| 2             | 0.147           | 0.643           | 0.21            | 1.68      | 1.3875           |
| 3             | 0.124           | 0.676           | 0.20            | 1.46      | 1.3876           |
| 4             | 0.122           | 0.698           | 0.18            | 0.77      | 1.388            |

TABLE -4.2.3 (ii)

(ii) 10% By weight

| Water Layer |                 |                 |                 |           |                  |
|-------------|-----------------|-----------------|-----------------|-----------|------------------|
| SL. No.     | X <sub>AA</sub> | X <sub>BA</sub> | X <sub>CA</sub> | %Wt. Salt | Refractive index |
| 1           | 0.599           | 0.151           | 0.25            | 6.13      | 1.359            |
| 2           | 0.698           | 0.102           | 0.20            | 7.3       | 1.352            |
| 3           | 0.731           | 0.089           | 0.18            | 7.37      | 1.349            |
| 4           | 0.783           | 0.077           | 0.14            | 8.34      | 1.346            |

| Butanol Layer |          |          |          |           |                  |
|---------------|----------|----------|----------|-----------|------------------|
| SL. No.       | $X_{AB}$ | $X_{BB}$ | $X_{CB}$ | %Wt. Salt | Refractive Index |
| 1             | 0.27     | 0.47     | 0.26     | 3.95      | 1.377            |
| 2             | 0.248    | 0.522    | 0.23     | 2.80      | 1.3772           |
| 3             | 0.223    | 0.577    | 0.20     | 2.48      | 1.378            |
| 4             | 0.215    | 0.61     | 0.175    | 1.11      | 1.380            |

TABLE -4.2.3 (iii)  
(iii) 15% By weight

| Water Layer |          |          |          |           |                  |
|-------------|----------|----------|----------|-----------|------------------|
| SL. No.     | $X_{AA}$ | $X_{BA}$ | $X_{CA}$ | %Wt. Salt | Refractive index |
| 1           | 0.615    | 0.125    | 0.26     | 10.1      | 1.346            |
| 2           | 0.632    | 0.118    | 0.25     | 11.45     | 1.344            |
| 3           | 0.676    | 0.089    | 0.235    | 12.63     | 1.342            |
| 4           | 0.698    | 0.082    | 0.22     | 12.87     | 1.340            |

| Butanol Layer |          |          |          |           |                  |
|---------------|----------|----------|----------|-----------|------------------|
| SL. No.       | $X_{AB}$ | $X_{BB}$ | $X_{CB}$ | %Wt. Salt | Refractive Index |
| 1             | 0.175    | 0.625    | 0.20     | 4.7       | 1.372            |
| 2             | 0.167    | 0.643    | 0.19     | 3.53      | 1.374            |
| 3             | 0.162    | 0.654    | 0.175    | 2.27      | 1.376            |
| 4             | 0.158    | 0.676    | 0.16     | 2.26      | 1.378            |

TABLE – 4.3

1. COSTANTS  $\ln A$  AND B IN MODIFIED CAMPBELL EQUATION

Table 4.3.1

| SALT    | % Wt. | $\ln A$ | B      |
|---------|-------|---------|--------|
| NO SALT | 0     | 0.0165  | 3.0335 |
| NaCl    | 5     | 0.0021  | 1.3544 |
|         | 10    | 0.0475  | 0.8598 |
|         | 15    | -0.1289 | 0.956  |
| KCl     | 5     | 0.1733  | 0.59   |
|         | 10    | 0.0632  | 0.7948 |
|         | 15    | -0.06   | 1.0    |

2. COSTANTS  $\ln A$  AND B IN HAND'S Plot

Table 4.3.2

| SALT    | % Wt. | $\ln A$ | B      |
|---------|-------|---------|--------|
| NO SALT | 0     | 0.0215  | 4.5726 |
| NaCl    | 5     | -0.0064 | 1.44   |
|         | 10    | 0.2445  | 0.8365 |
|         | 15    | -0.0578 | 0.557  |
| KCl     | 5     | 0.2324  | 1.2937 |
|         | 10    | 0.0808  | 1.1479 |
|         | 15    | 0.0016  | 0.7517 |

TABLE-4.4

## 1. CONSTANTS a, b, c, d IN MODIFIED CAMPBELL EQUATION

Table – 4.4.1

| SALT    | % Wt. | a      | b       | c      | d       | Regration Co-efficient |
|---------|-------|--------|---------|--------|---------|------------------------|
| NO SALT | 0     | 0.0165 |         | 3.0335 |         | 0.8588                 |
| NaCl    | 5     | 0.0165 | -0.0028 | 3.0335 | -0.335  | 0.9957                 |
|         | 10    | 0.0165 | 0.0031  | 3.0335 | -0.217  | 0.9888                 |
|         | 15    | 0.0165 | -0.0096 | 3.0335 | -0.1358 | 0.9751                 |
| KCl     | 5     | 0.0165 | 0.0314  | 3.0335 | -0.4887 | 0.9818                 |
|         | 10    | 0.0165 | 0.00467 | 3.0335 | -0.2238 | 0.9743                 |
|         | 15    | 0.0165 | -0.0051 | 3.0335 | -0.1355 | 1                      |

## 2. CONSTANTS a, b, c, d IN EISEN-JOFFE EQUATION

| SALT    | % Wt. | a      | b       | c      | d       | Regration Co-efficient |
|---------|-------|--------|---------|--------|---------|------------------------|
| NO SALT | 0     | 0.0215 |         | 4.5726 |         | 0.8824                 |
| NaCl    | 5     | 0.0215 | -0.0055 | 4.5726 | -0.6265 | 0.9901                 |
|         | 10    | 0.0215 | 0.0223  | 4.5726 | -0.3736 | 0.8777                 |
|         | 15    | 0.0215 | -0.0053 | 4.5726 | -0.2677 | 0.9113                 |
| KCl     | 5     | 0.0215 | 0.0422  | 4.5726 | -0.6557 | 0.9874                 |
|         | 10    | 0.0215 | 0.0059  | 4.5726 | -0.3425 | 0.9655                 |
|         | 15    | 0.0215 | -0.0013 | 4.5726 | -0.255  | 0.9897                 |



TABLE – 4.5

COMPARISION BETWEEN  $X_{CB}$  – OBSERVED AND  $X_{CB}$  CALCULATED

Table 4.5.1

## 1. SALT : SODIUM CHLORIDE (NaCl)

| % Wt. Salt                        |                      | Campbell Equation      |         | Eisen-Joffe Equation              |         |
|-----------------------------------|----------------------|------------------------|---------|-----------------------------------|---------|
|                                   | $X_{CB}$<br>observed | $X_{CB}$<br>Calculated | % Error | $X_{CB}$<br>Calculated            | % Error |
| 5                                 | 0.18                 | 0.063                  | 65      | 0.0634                            | 64.77   |
|                                   | 0.12                 | 0.0385                 | 67.9    | 0.0374                            | 68.83   |
|                                   | 0.08                 | 0.0197                 | 75.4    | 0.0162                            | 79.75   |
|                                   | 0.07                 | 0.0178                 | 74.5    | 0.0142                            | 79.71   |
| 10                                | 0.3                  | 0.391                  | 30.3    | 0.447                             | 49.0    |
|                                   | 0.29                 | 0.373                  | 28.62   | 0.401                             | 38.27   |
|                                   | 0.28                 | 0.362                  | 29.3    | 0.391                             | 39.64   |
|                                   | 0.27                 | 0.350                  | 29.63   | 0.383                             | 41.85   |
| 15                                | 0.195                | 0.261                  | 33.85   | 0.0426                            | 78.15   |
|                                   | 0.165                | 0.245                  | 48.48   | 0.0433                            | 73.75   |
|                                   | 0.15                 | 0.227                  | 51.33   | 0.0394                            | 73.73   |
|                                   | 0.13                 | 0.212                  | 63.07   | 0.382                             | 70.61   |
| Standard Deviation-0.1385         |                      |                        |         | Standard Deviation0.1806          |         |
| Root Mean Square Deviation-0.0808 |                      |                        |         | Root Mean Square Deviation-0.1292 |         |

Table 4.5.2

## 2. POTASSIUM CHLORIDE (KCl)

| % Wt. Salt                        | Campbell Equation           |                               |         | Eisen-Joffe Equation              |         |
|-----------------------------------|-----------------------------|-------------------------------|---------|-----------------------------------|---------|
|                                   | X <sub>CB</sub><br>observed | X <sub>CB</sub><br>Calculated | % Error | X <sub>CB</sub><br>Calculated     | % Error |
| 5                                 | 0.24                        | 0.405                         | 68.75   | 0.0756                            | 68.5    |
|                                   | 0.21                        | 0.310                         | 47.61   | 0.049                             | 76.66   |
|                                   | 0.20                        | 0.223                         | 11.5    | 0.0203                            | 89.85   |
|                                   | 0.18                        | 0.109                         | 39.44   | 0.0433                            | 75.94   |
| 10                                | 0.26                        | 0.384                         | 47.69   | 0.207                             | 20.38   |
|                                   | 0.23                        | 0.322                         | 40.0    | 0.149                             | 35.21   |
|                                   | 0.20                        | 0.295                         | 47.5    | 0.138                             | 31.0    |
|                                   | 0.175                       | 0.242                         | 38.28   | 0.101                             | 42.28   |
| 15                                | 0.20                        | 0.226                         | 13.0    | 0.327                             | 63.5    |
|                                   | 0.19                        | 0.217                         | 14.21   | 0.321                             | 68.94   |
|                                   | 0.175                       | 0.204                         | 16.57   | 0.296                             | 69.14   |
|                                   | 0.16                        | 0.192                         | 20.0    | 0.285                             | 78.13   |
| Standard Deviation-0.0813         |                             |                               |         | Standard Deviation-0.1103         |         |
| Root Mean Square Deviation-0.0834 |                             |                               |         | Root Mean Square Deviation-0.1245 |         |

## RESULT AND DISCUSSION

The liquid-liquid equilibrium for the given ternary system was observed at atmospheric pressure and a temperature of 25<sup>0</sup>C. The ternary solubility data and the tie line data are determined in the presence of NaCl, KCl at 5%, 10% and 15% concentration for the system water + acetone + 1-butanol at same temperature. It had seen from the diagram that the addition of salts accelerate the distribution in favour of 1-butanol layer especially at higher salt concentration. The solubility decreases in presence of the salt and increases the heterogeneous zone of the system. Heterogeneous area plays an important role in liquid-liquid equilibrium. In the supplied system, it was seen that the areas of the solubility curve are more in case of salt addition than that of without salt. More acetone is shifted towards the butanol phase with increasing salt concentrations. This process is generally known as “salting out effect” and is caused by the fact that the presence of high amount of hydrated ions decreases the availability of the water molecules in the aqueous phase to the salvation of other solvents. The concentration of acetone in organic phase increases by presence of salts and hence enlargement of the two phase region occurred. These process increase with salt concentration and are maximum at salt saturation. From the binodial curve it is seen that the salting out effect is more in NaCl. Hence the order of effectiveness of salt was as follows.

NaCl > KCl. The orders of effectiveness of the salts based on the salt effect parameter were derived from Eisen – Joffee Equation and modified Campbell equation.

## CHAPTER – 5

### CONCLUSION

The liquid-liquid equilibrium diagram for ternary system water + 1-butanol + acetone was determined at 25<sup>0</sup>C. The effects of salt like NaCl and KCl on the ternary system at different concentrations were observed at the same temperature. Eisen – Joffe and Campbell correlations are used for the determination of the corresponding parameters for the given system with and without salt, which are appropriate for interpolation of the equilibrium data. In case of all the systems containing dissolved salt, under study it is observed that at lower concentration modified Campbell equation gives more error. From the present experiment it was seen that modified Campbell equation correlate better in presence of NaCl compared to KCl. The experimental results lead to the conclusion that a salting out effect exists for all the salts under study, increasing for higher salt concentrations. In conclusion it may be indicated that concerted efforts on the observations of the salt effect on the distribution of a solute between two partially miscible liquids have a potential scope for engineering applications.

The use of solid inorganic salt in place of liquid separating agent in extraction process has great advantages. It is because by use of small amount of solid salt bring about a substantial change in phase equilibrium in ternary liquid system. This fact is observed and conformed in case of ternary system under investigation. Thus it is concluded that this technique can be used effectively for extraction of liquid (solute) using solid salt.

## REFERENCES

- [1] Gomis Vicente, Prats Daniel, Ruiz Francisco, Asensi Juan Carlos, Reus Francisco, quaternary liquid-liquid equilibrium: water-acetic acid-2-butanone-cyclohexane at 25°C, Elsevier, Fluid Phase Equilibria 106 (1995), 203 -211.
- [2] Hasseine A., Meniai A H, Korichi M, salting out effect of single salt NaCl and KCl on the LLE of the system(Water + acetone + toluene), (Water + cyclohexane + 2-propanol) and (Water + xylene + methanol), science direct, Desalination 242 (2009), 264-276.
- [3] Chen Jui Tang, Chen Ming-Chung, salt effect on LLE for the ternary system (water + N-methyl-2-pyrrolidone + 1-pentanol), science direct, Fluid Phase Equilibria 266(2008), 1-7.
- [4] Bourayou N., Meniai A H, Experimental and theoretical study of the influence of salt on liquid phase equilibrium for totally miscible organic compound with water, science direct, Desalination 185 (2005), 473-481.
- [5] Pai M. U., Rao K. M., salt effect on liquid-liquid equilibria in the ethyl Acetate-ethyl alcohol-water system J. Chem. Engg. Data 11 (1966), 353-356.
- [6] Santos Fania S., d'Avila Saul G., Aznar Martin, salt effect on liquid-liquid equilibrium of water + 1-butanol + acetone: experimental determination and thermodynamic modeling, science direct, fluid phase equilibria 187-188 (2001), 265-274.
- [7] Vakili-Nezhaad G.R., Mohsen-Nia M., Taghikhani V., salting out effect of NaCl and KCl on the ternary LLE data for the systems of (water + propionic acid + isopropyl methyl ketone) and of (water + propionic acid + isobutyl methyl ketone), science direct, J. Chem. Thermodynamics 36 (2004), 341 – 348.
- [8] Erol Ince, (Liquid + liquid) equilibria of the (water + acetic acid + dibasic esters mixture) system, science direct, J. Chem. Thermodynamics 38(2006), 1669-1674.
- [9] Hung Shih-Bo, Lin Ho-Mu, Yu Cheng-Ching, Huang Hsiao-Ping, Lee Ming-Jer, Liquid–liquid equilibria of aqueous mixtures containing selected dibasic esters and/or methanol, science direct, Fluid Phase Equilibria 248 (2006), 174–180.
- [10] Hu Mancheng, Wang Meixia, Li Shu ni, Jiang Yucheng, Guo Haiyan, Liquid-liquid equilibrium for water + 1-propanol/2-propanol + potassium chloride + cesium chloride quaternary systems at 298.1K, science direct,fluid phase Equilibria 263 (2008), 109-114.
- [11] Santos G. R, d'Avila S.G, Aznar M., salt effect of KBr on liquid-liquid equilibrium of water/ethanol/1-pentanol system, Brazilian journal of chemical engineering, 17(2000), 721-734.

- [12] Tan T.C., Kannangare k.K.D.D.S., Liquid-liquid equilibria of water/1-propanol/methyl ethyl ketone/potassium chloride, science direct, fluid phase Equilibrium 190 (2001), 179-189.
- [13] Solimo Horacio N., Bonatti Carlos M., Zurita Jose L., de Doz Monica B. Gramajo , Liquid-liquid equilibria for the system water + propionic acid + 1- butanol at 303.2K, Effect of addition of sodium chloride, Elsevier, Fluid-Phase Equilibria 137 (1997), 163-172.
- [14] R. Pedraza, F. Ruiz, M.D. Saquete, V. Gomis, Liquid-liquid-solid equilibrium for the water + sodium chloride + potassium chloride + 1- butanol quaternary system at 25<sup>0</sup>C, Science direct, Fluid Phase Equilibria 216 (2004), 27–31.
- [15] Tan T.C., Aravinth S., Liquid-liquid equilibria of water/acetic acid/1- butanol system-effects of sodium(potassium) chloride and correlation, Elsevier, Fluid Phase Equilibria 163(1999), 243–257.
- [16] Othmer Donald f., Tobias Philip E., Liquid-liquid extraction data – tie line correlation, Industrial & Engineering Chemistry, 34 (6) (1942), 693-696.
- [17] Eisen E.O., Joffe J., Salt effect in liquid-liquid equilibrium, Journal of Chemical & Engineering Data, 11 (4) (1966), 480-484.
- [18] Govindarajan M., Sabarthnam P.L., Salt effect on liquid-liquid equilibrium of the methyl isobutyl ketone – acetic acid – water system at 35<sup>0</sup>C, Elsevier, fluid phase equilibria, 108 (1995), 269- 292.
- [19] Campbell H. R., Shallal A.K., Bauer H.H., Salting effects in several alcohol- electrolyte-water systems, Journal of Chemical & Engineering Data, 15 (1970), 311-312.
- [20] Desai M.L., Eisen E. O., Salt effects in liquid-liquid equilibria, Journal of Chemical & Engineering Data, 16(2) (1971), 200-202.
- [21] Acharya Arun, Salt effect on liquid-liquid equilibrium for ternary system n- butanol + n – propanol + water, M. Tech. Thesis, Submitted to department of chemical Engg. Rourkela, June 2004.
- [22] Swabb, L.E., Mongan, E.L., Solvent extraction from aqueous solution, Effect of addition of inorganic salts, Chem. Eng. Prog. Sym. Ser. 48 (1952), 40-45.
- [23] Campbell J.A., Distribution equation, Industrial & Engineering Chemistry, 36 (1944), 1158-1161.

[24] Hand D.B., The distribution of consolute liquid between two immiscible liquids, J. Phys. Chem., 34 (1930), 1961-2000.

[25] Setschenow J., Z. Phys. Chem., 4 (1889), 117.